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Amirhossein Amirsoleymani
University of Windsor

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Prediction of the Dependence of Viscosities of Multi-component Non-electrolyte Liquid Mixtures on Concentration

By

Amirhossein Amirsoleymani

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2021

Prediction of the Dependence of Viscosities of Multi-component Non-electrolyte Liquid Mixtures on Concentration

By

Amirhossein Amirsoleymani

APPROVED BY:

N. Zamani
Department of Mechanical, Automotive & Materials Engineering

R. Balachandar
Department of Civil and Environmental Engineering

A. Asfour, Advisor
Department of Civil and Environmental Engineering

February 11, 2021

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ABSTRACT

The present study reports the mathematical development of a generalized predictive McAllister-type 4-body and 5-body interaction models which are applicable to multi-components systems. The reported models were extended and made predictive on the basis of the earlier work of Asfour and co-workers (1991, 1992, 1998, 2000a, and 2000b). The models were validated using an extensive database available from the literature including all types of multi-component systems with components having different molecular structures at different temperatures.

A total of 4226 experimental data points representing binary, ternary, quaternary, and quinary were used in validating the model.

The McAllister 4-body and 5-body interaction models gave satisfactory results. The *pseudo*-binary model (Wu and Asfour, 1992) was used with both the McAllister 4-body and 5-body interaction models. The *pseudo*-binary model reduces the number of parameters to two parameters regardless of the number of components in a system. The predictive capabilities of the 4-body, 5-body interaction models and the *pseudo*-McAllister binary models were compared with those of the 3-body generalized interaction model (Nhaesi and Asfour, 2000a) and the GC-UNIMODE model (Cao *et al.* 1993) with varying degrees of success.

DEDICATION

I dedicate this thesis to my family. Thanks for everything they have done for me.

ACKNOWLEDGEMENTS

The present work is the outcome of research in the Environmental Engineering Program, University of Windsor. The present thesis is based on the topic of the kinematic viscosity of non-electrolyte liquid systems. I gratefully acknowledge the people who assisted me along this path.

First and foremost, I would like to express my gratitude and appreciation to Dr. Abdul-Fattah Asfour, my supervisor, for his invaluable guidance and constant support throughout different steps of this work. He means like a father for me, and his guidance helped me in research. His way of thinking inspired me to approach the problem in different ways. Certainly, it was an honour to be his student.

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My endless appreciation goes to my family, my mother, my father and my beautiful sister, Negin Amirsoleimani, who always supported me regardless of the situation and any any condition and always endowed me with infinite love, encouragement and patience. I also want to express my sincere thanks to my grandmother and grandfather, whom I wish their souls will rest in peace for their unconditional love and support.

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CHAPTER 1

INTRODUCTION

1.1. General

In engineering, resistance to deformation of fluids is called viscosity, which is used in a different application. The shear stress and velocity gradient (shear rate) for Newtonian fluids are related to each other according to Newton's law as follows:

$$\tau = -\eta \frac{d\mathrm{v}}{dy} \tag{1.1}$$

The force applied to the fluid per unit area is the shear stress, τ, which is shown in Equation (1.1). The absolute viscosity of the mixture depends on several factors such as, temperature and pressure. Lack of knowledge regarding the exact behaviour of components in systems motivates researchers to determine the properties of solutions. Different behaviours of mixtures is due to several causes such as intermolecular forces and the difference in sizes of the molecules in liquid systems. Asfour (1979) suggested breaking-down liquid mixtures into three categories; *viz*., (i) *n*-alkane solutions, (ii) regular mixtures, and (iii) associated solutions. This classification has led to series of publications by Asfour and co-workers; e.g., Wu and Asfour (1992), Nhaesi and Asfour (1998), Nhaesi and Asfour (2000 a and b), Al-Gherwi and Asfour (2005), Nhaesi, *et al*. (2006), Hamzalouia and Asfour (2012 and 2013) and Mohajerani (2013).

Mathematical models in this area can be classified into two categories; *viz.,* (i) correlative and (ii) predictive. The correlative models contain adjustable parameter(s) where their values are needed to calculate the dependence of viscosity on composition. Determination of the values of such parameters require experimental data. The more data one has results im more precise calculations, This obviously defeats the purpose of having a model since obtaining experimental data is both costly and time consuming. On the other hand, predictive models do not need extensive experimental data especially in that the values of the model parameters can be calculated from molecular and pure component propertis.

There are different types of Eyring-based models, like Local Composition models (LC) and the McAllister interaction models. Eyring's absolute rate theory was utilized by McAllister (1960) to develop a correlative model for calculating the dependence of the kinematic viscosity of liquid mixtures on composition. However, this model was developed only for binary liquid systems.. Therefore, Chandramouli and Laddha (1963) extended the model to ternary systems, but their model was still correlative in nature. Although the McAllister model correlates data by its adjustable parameters very well, the parameters were the main deficiency because they need experimental data for the determination of their numerical values.

By using pure component viscosities and molecular parameters, Asfour *et al.* (1991) proposed a new technique for predicting the McAllister model parameters for the case of *n*-alkane binary systems. Thus, converting the correlatve McAllister model for the first time into a predictive one. Nhaesi and Asfour (1998) extended this technique to make the model compatible with a solution containing regular components by introducing the concept of *Effective Carbon Number* (*ECN*).. Following that, Nhaesi and Asfour (2000a) reported the development of a generalized multi-component three-body collision predictive McAllister model. Those authors employed an extensive database from the literature to test their model. The model was very successful in predicting the viscosities of reular solutions and clearly outperformed other models available from the litearture.

In the present study, six predictive viscosity models were subjected to testing of their predictive capabilities. Three models were developed and are being reported in the present study;

viz., the McAllister five-body (Mc-5b), the McAllister four-body (Mc-4b) and their *pseudo*-binary models. These three developed models were compared with the generalized McAllister three-body collision that was reported by Nahesi and Asfour (2000a) and the GC-UNIMOD model that was reported by Cao *et al.* (1993). An extensive database was compiled from the literature and used to test and compare the prediction capabilities of the models using the average absolute deviation as a criterion for comparison. A total of 4226 points of binary, ternary, quaternary and quinary systems were employed for the testing. Moreover, a new technique is being proposed for calculating more precisely the values of the interaction parameters of the McAllister *pseudo*-binary models. Herein, mixtures were classified into four categories; *viz*., (a) *n*-alkane, (b) 1-alkanols, (c) regular solutions (d) regular solutions + 1-alkanols.

1.2. Objectives

The experimental data employed in this study for testing the models were gathered from reliable literature sources. The present study can be divided into two parts. The objectives of the first part of the study are:

(i) To develope a generalized Mc-4b model for multi-component liquid mixtures.

(ii) To develope the Asfour and co-workers'techniques for the determination of each type of generalized four-body collision McAllister model parameters within the specific category of data.

(iii) To vaidate the generalized model and techniques used for the calculation of the model parameters.

(iv) To employ the *pseudo*-binary model with the generalized McAllister four-body model in order to reduce the number of parameters to be predicted.

(v) To compare the four-body McAllister model and *pseudo*-binary model results with three other predictive methods; *viz*., the GC-UNIMOD, the McAllister three-body and the *pseudo-binary* McAllister three-body models.

The objectives of the second part of the study are:

(i) To convert the Mc-5b binary interaction model into a predictive model and to test the model using experimental data on regular binary systems.

(ii) To compare the Mc-5b binary model with other types of predictive McAllister models.

(iii) To propose a new technique of determining the *pseudo*-binary interaction parameters in multi-component systems for the McAllister *pseudo*-binary models and testing the technique against the conventional method of prediction in those models.

1.3. Contributions and Significance

The following contributions have been made during the course of the present study:

- Classification of the gathered data based on the component type in the specific mixture.
- Converting the Mc-4b model for predicting the viscosity of ternary, quaternary and quinary systems over the entire composition range for an extensive database, including regular systems by employing the Asfour *et al*. (1991) technique.
- Converting the Mc-5b binary interaction model into a predictive model and testing its predictive capability..
- The *pseudo*-binary model was applied to the different versions of the predictive McAllister model, which reduces the number of parameters to be predicted in the case of multi-component mixtures. This dramatically reduces the time and complexity of calculations.

- In addition, a new technique was proposed for improving the results of *pseudo*-binary McAllister models.

CHAPTER 2

LITERATURE SURVEY

2.1. General

Viscosity is a transport property that is important for solving engineering problems. According to Chapter 1, suitable mathematical models are essential for engineering design calculations. The present study is mainly focused on the mathematical modelling for predicting the dependence of viscosity on composition. Semi-theoretical and empirical models represent another approach to classify the mathematical models. The first approach requires both theory and experimental data whereas the second approach is correlative and normally needs extensive experimental data; e.g., the Allan and Teja (1991) and the Grunberg and Nissan (1949) correlations. Previous studies show that semi-theoretical models are more valuable than empirical models. The semi-theoretical models are our target for the present study. The present chapter presents a detailed explanation of the available methods for determining the viscosities of liquid mixtures.

2.2. Semi-theoretical Models of Viscosity of Liquid Mixtures

The combination of a series of formulations with dependent and independent parameters results in creating a semi-theoretical class of models. The contained parameters in these models can be determined by the existing experimental data. The McAllister model (1960) is a classic example of those models which was developed on the basis of the absolute rate theory.

Eyring (1936) assumed that fluids consist of different layers of molecules. The necessary condition for the movement of a single molecule is the existence of free space between them, but it is not sufficient as the expenditure of energy will be needed. Based on Figure (2.1 a), there would be a vacant site in the second layer for receiving molecules when shear stress is applied to the first layer. The vacant position remains available by the movement of molecules from the equilibrium position to the next layer. The required energy for the movement of molecules between adjacent layers is called the potential energy barrier, ΔG_0^*, shown in Figure (2.1 b). Without forces applied on the fluid, the movement rate in the forward and backward directions is equal, then the jump frequency in the forward and backward directions calculated by the following equation:

$$r_0 = \frac{KT}{h} exp\left(-\frac{\Delta G_0^*}{KT}\right) \tag{2.1}$$

Where *T* is the absolute temperature, *K* is the Boltzmann constant, and *h* is Planck's constant. According to Figure (2.1), assuming λ_1 *is* a distance between two adjacent layers undergoing shear stress and $\lambda_2\lambda_3$ is an average area occupied with a single molecule. λ_2 and λ_3 are the average distances between neighbouring molecules and the average distance between molecules normal to the direction of movement. Also, assuming λ is the available space between the molecules. If the shear stress exerted on the fluid, the movement energy in the forward and backward directions are varied. Therefore, there would be losses of energy which is equal to $\lambda_2\lambda_3\frac{\lambda}{2}$. The forward and backward rates of jumping can be calculated as follow:

$$r_f = \frac{KT}{h} exp\left(-\frac{\Delta G_0^* - f\lambda_2\lambda_3(\lambda/2)}{KT}\right) \tag{2.2}$$

$$r_b = \frac{KT}{h} exp\left(-\frac{\Delta G_0^* + f\lambda_2\lambda_3(\lambda/2)}{KT}\right) \tag{2.3}$$

Therefore, the net is the total rate of jumping:

$$r_t = f\lambda_2\lambda_3(\lambda/h)\ exp\left(-\frac{\Delta G_0^*}{KT}\right) \tag{2.4}$$

By the distance of λ_1, the velocity gradient between the two layers is obtained:

$$\frac{dy}{dx} = \frac{\lambda_r}{\lambda_1} \tag{2.5}$$

Where λ is the distance per jump, and r is the number of jumps per second. Based on Newton's law:

$$f = -\mu\frac{dv}{dx} = -\mu\frac{\lambda_r}{\lambda_1} \tag{2.6}$$

Then, the absolute viscosity of the liquid is:

$$\mu = \frac{\lambda_1 h}{\lambda_r \lambda_2 \lambda} e^{\frac{\Delta G^*}{RT}} \tag{2.7}$$

By considering $\lambda = \lambda_1$ and identifying $\lambda_1\ \lambda_2\ \lambda_3$ as the effective volume of the molecule, Equation (2.7) converts to:

$$\mu = \frac{Nh}{V} e^{\frac{\Delta G^*}{RT}} \tag{2.8}$$

Therefore, the kinematic viscosity relation is formed as,

$$v = \frac{\mu}{\rho} = \frac{Nh}{M} e^{\frac{\Delta G^0}{RT}} \tag{2.9}$$

Where M, N, ρ and ΔG^0 are molecular weight, Avogadro's number, density and the molar activation of viscose flow, respectively.

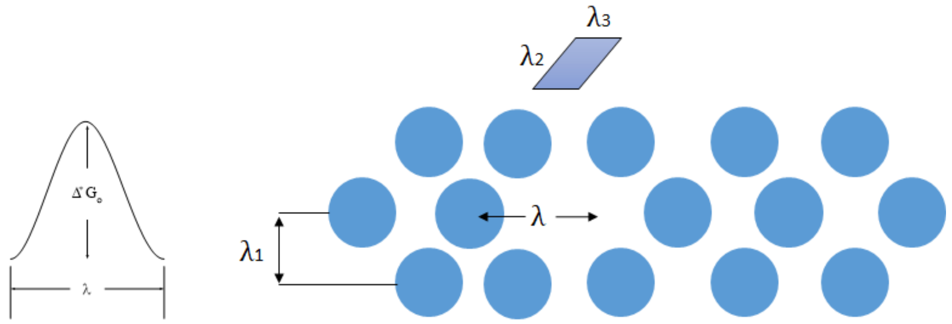


Figure 2.1. The Eyring molecular model of liquid viscosity

2.2.1. McAllister's three-body collision model (binary)

McAllister (1960) developed two new models by considering different types of interactions, three-body collision and four-body collision, of molecules based on Eyring's rate theory. By the correlation of several systems, He suggested using the McAllister three-body collision model for the binary systems containing components with a radii ratio of between 1 to 1.5. The interactions are assumed in two directions in a simple plane. In this model, the mixture is considered with two components of (a) and (b). The different types of intermolecular interactions between these two components are shown in Figure 2.2.

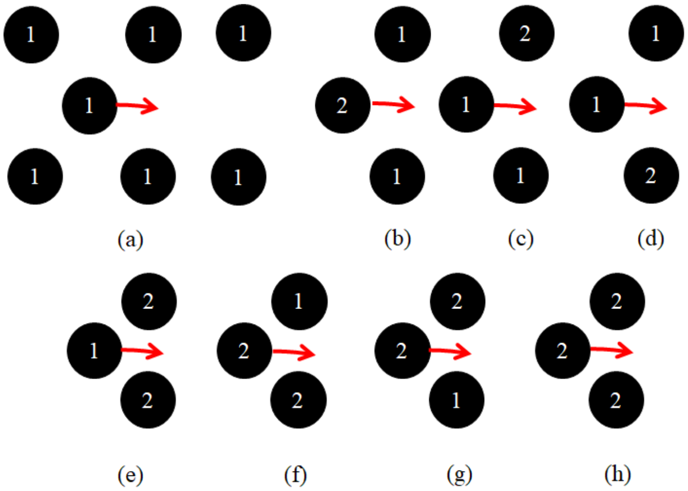


Figure 2.2. Different types of molecular interactions involved in binary mixtures for three-body collision model.

Each type of occurrence has its specific energy of activation and the total probability of each interaction just depends on the mole fractions of components. McAllister found a relation for the total energy of activation in the hypothetical solution as below:

$$\Delta^* G = x_a^3 \Delta^* G_a + x_a^2 x_b \Delta^* G_{aba} + 2x_a^2 x_b \Delta^* G_{aab} + x_a x_b^2 \Delta^* G_{bab} + 2x_a x_b^2 \Delta^* G_{abb} + x_b^3 \Delta^* G_b \tag{2.10}$$

On the right-hand side, each term shows the fraction of total occurrence, as a function of compositions, multiplied by the activation energy. Table 2.1 indicates the interaction type and corresponding energy of activation and the total possibility of occurrence in the hypothetical mixture. The subscript *i* is the component type *a* or *b,* and *x* is the composition of molecules in the mixture.

Table 2.1. Six Types of interactions in a binary mixture of molecules (a) and (b), their relating free energy of activation along with a fraction of total occurrence for the three-body collision model.

Interaction type	*a-a-a*	*a-b-a*	*b-a-a* *a-a-b*	*b-a-b*	*b-b-a* *a-b-b*	*b-b-b*
Energy of activation	$\Delta^{*}G_{a}$	$\Delta^{*}G_{aba}$	$\Delta^{*}G_{aab}$	$\Delta^{*}G_{bab}$	$\Delta^{*}G_{abb}$	$\Delta^{*}G_{b}$
The fraction of total occurrence	x_a^3	$x_a^2 x_b$	$2x_a^2 x_b$	$x_a\ x_b^2$	$2x_a\ x_b^2$	x_b^3

To make the model simple, additional assumptions were adopted,

$$\Delta^{*}G_{aba} = \Delta^{*}G_{aab} = \Delta^{*}G_{ab} \quad \leftrightarrow \quad \Delta^{*}G_{ab} = \frac{(\Delta^{*}G_{aba} + 2\Delta^{*}G_{aab})}{3} \tag{2.11}$$

$$\Delta^{*}G_{bab} = \Delta^{*}G_{abb} = \Delta^{*}G_{ba} \leftrightarrow \Delta^{*}G_{ba} = \frac{(\Delta^{*}G_{bab} + 2\Delta^{*}G_{bba})}{3} \tag{2.12}$$

Then, Equation (2.10) can be rewritten as,

$$\Delta^{*}G = x_a^3\Delta^{*}G_a + 3x_a^2x_b\Delta^{*}G_{ab} + 3x_ax_b^2\Delta^{*}G_{ba} + x_b^3\Delta^{*}G_b \tag{2.13}$$

To eliminate the energy of the activations, the corresponding viscosity was formed based on the Equation (2.14).

$$v = \frac{hN}{M_{average}} e^{\frac{\Delta^{*}G}{RT}} \tag{2.14}$$

Viscosity of the pure component *i* is expressed as follows:

$$v_i = \frac{hN}{M_i} e^{\frac{\Delta^{*}G_i}{RT}} \tag{2.15}$$

For interactions type between molecules *i* and *j*,

$$v_{ij} = \frac{hN}{M_{ij}} e^{\frac{\Delta^{*}G_{ij}}{RT}} \tag{2.16}$$

Where the following relation obtains M_{ij},

$$M_{ij} = \frac{2M_i + \ M_j}{3} \tag{2.17}$$

By substituting Equation (2.13) into Equation (2.14), the kinematic viscosity is obtained as a function of compositions and energies of activation,

$$v = \frac{hN}{M_{ave}}\, e^{\frac{\left[x_1^3 \Delta^* G_1 + 3x_1^2 x_2 \Delta^* G_{12} + 3x_1 x_2^2 \Delta^* G_{21} + x_2^3 \Delta^* G_2\right]}{RT}} \tag{2.18}$$

By taking the logarithms of Equations (2.14) through (2.17) and substituting in Equation (2.18), the kinematic viscosity was obtained as a function of interaction parameters and compositions.

$$lnv = x_a^3 \ln v_a + 3x_a^2 x_b \ln v_{ab} + 3x_a x_b^2 \ln v_{ba} + x_b^3 \ln v_b - \ln\left[x_a + \frac{x_b M_b}{M_a}\right]$$
$$+3x_a^2 \ln\left[\frac{\left(2 + \frac{M_b}{M_a}\right)}{3}\right] + 3x_a x_b^2 \ln\left[\frac{\left(1 + \frac{2M_b}{M_a}\right)}{3}\right] + x_b^3 \ln[M_b/M_a] \tag{2.19}$$

Equation (2.19) is a polynomial cubic equation with two adjustable parameters; v_{ab} and v_{ba}, that can be correlated in the model using experimental data. This model is called the three-body interaction McAllister model.

2.2.2. <u>The McAllister four-body model (binary)</u>

McAllister also derived the McAllister model for the four-body collision of molecules of binary mixtures. He suggested using the McAllister four-body interaction model for binary systems containing components with a radiuii ratio of over 1.5. The four-body method is almost like three-dimensional treatment. Figure (2.3) shows the different forms of interaction between two molecules 1 and 2.

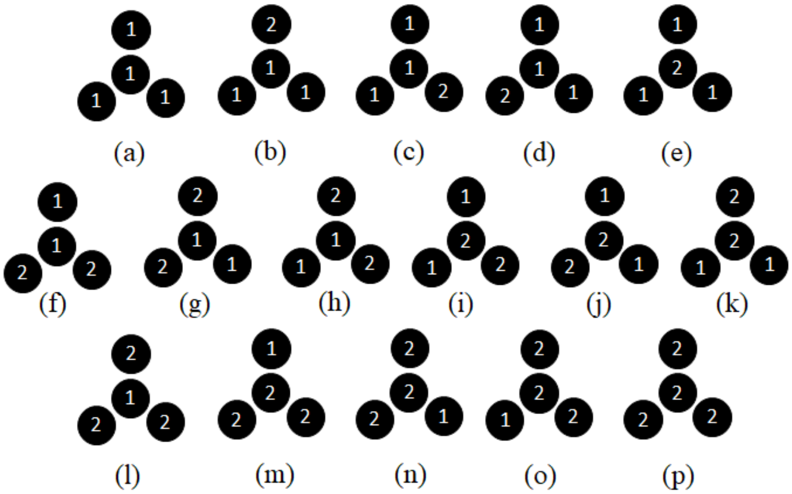


Figure 2.3. Different types of molecular interactions involved in binary mixtures for the four-body collision model.

Similar to the three-body approach, a quadratic model was derived by McAllister (1960). The interaction model obtained is shown in Equation (2.20) given below,

$$lnv = x_a^4 \ln v_a + 4x_1^3 x_2 \ln v_{aaab} + 6x_1^2 x_2^2 \ln v_{aabb} + 4x_1 x_2^3 \ln v_{bbba} + x_b^4 \ln v_b \qquad (2.20)$$

$$- \ln\left[x_a + \frac{x_b M_b}{M_a}\right] + 4x_a^3 x_b \ln\left[\frac{\left(3 + \frac{M_b}{M_a}\right)}{4}\right] + 6x_a^2 x_b^2 \ln \frac{\left(1 + \frac{M_b}{M_a}\right)}{2} + 4x_1 x_2^3 \ln\left[\frac{(1 + 3M_b/M_a)}{4}\right]$$

The above equation contains three adjustable parameters, namely, v_{aaab}, v_{aabb}, and v_{bbba}, which can be determined by fitting experimental binary system data to the above equation.

2.2.3. <u>The McAllister three-body model (ternary)</u>

Chandermouli and Laddha (1963) extended the McAllister model to be applicable to ternary systems. They presented the model as follows:

$$lnv = x_a^3 \ln v_a + x_b^3 \ln v_b + x_c^3 \ln v_c + 3x_a^2 x_b \ln v_{ab} + 3x_a^2 x_c \ln v_{ac} + 3x_b^2 x_a \ln v_{ba} + 3x_b^2 x_c \ln v_{bc}$$

$$+6x_a x_b x_c \ln v_{abc} - \ln(x_a M_a + x_b M_b + x_c M_c) + x_a^3 \ln M_a + x_b^3 \ln M_b + x_c^3 \ln M_c \qquad (2.21)$$

$$+3x_a^2 x_b \ln \frac{(2M_a + M_b)}{3} + 3x_a^2 x_c \ln \frac{(2M_a + M_c)}{3} + 3x_b^2 x_a \ln \frac{(2M_b + M_a)}{3} + 3x_b^2 x_c \ln \frac{(2M_b + M_c)}{3}$$

$$+3x_c^2 x_a \ln \frac{(2M_c + M_a)}{3} + 3x_c^2 x_b \ln \frac{(2M_c + M_b)}{3} + 6x_a x_b x_{3c} \ln \frac{M_a + M_b + M_c}{3}$$

where M_a, M_b and M_c are the molecular weight of components a, b and c. Models include two types of interaction; namely, (i) binary interaction parameters, v_{ij}, and (ii) a ternary interaction parameter, v_{ijk}. They calculated the value of v_{ij} by fitting experimental data of viscosity of three pure components to calculate the binary interaction parameters of v_{ab}, v_{ba}, v_{ac}, v_{ca}, v_{bc} and v_{cb}. Also, the least-square method was used for obtaining the value of the ternary interaction parameter, v_{abc}.

2.2.4. The Generalized McAllister three-body model

The first attempt to generalize the McAllister three-body model was reported by Dizechi and Marschall (1982). Their generalized model contained two constants, *C* and *Z,* which were proposed to account for the dependence of the adjustable parameters on temperature. They tested their model on twelve binary and ternary polar liquid mixtures at different temperatures, resulting in improved prediction of those points. Soliman and Marschall (1990) tried to decrease the number of correlated parameters as it would cause the overfitting problem in such a model. They utilized the least-square approach to fit the model to the experimental data. The results showed a better performance of the Soleiman-Marschall model compared to the Dizechi-Marschall model in some cases. All such models that were based on the McAllister model were not capable of predicting the kinematic viscosity of multi-component mixtures of more than three components. Nhaesi and Asfour (2000a) developed and reported a generalized form of the McAllister model for multi-component systems. However, the problem was existance of many different types of interaction parameters in the model. In order to overcome this problem, different assumptions were made by Nhaesi and Asfour (2000a), to reduce the number of interaction parameters. They assumed that only three-body collision takes place in that case; which is similar to the assumption made by Chandermouli and Laddha (1963) in developing their ternary system McAllister-type model. The Nhaesi-Asfour multi-component generalized model contains binary and ternary interaction parameters. In the first step, the additive feature of the activation energy of kinematic viscosities was used to determine the activation energy of mixtures as shown in Equation (2.22) as follows:

$$\Delta G_m = \sum_{i=1}^{n} x_i^3\,\Delta G_i + 3\sum_{i=1}^{n}\sum_{j=1}^{n} x_i^2\,x_j \Delta G_{ij} + 6\sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n} x_i x_j x_k\,\Delta G_{ijk} \tag{2.22}$$

Where i, j and k are the mixture components, and n is the number of components. In order to simplify the model, the following two additional assumptions were made:

$$\Delta G_{iji} = \Delta G_{iij} = \Delta G_{ij} \tag{2.23}$$

$$\Delta G_{jij} = \Delta G_{ijj} = \Delta G_{ji} \tag{2.24}$$

The kinematic viscosities of the pure components, binary and, ternary interaction parameters were related to the free energy of activation by Arrhenius-type relations. Pure and binary kinematic viscosities were replaced with Equations (2.15) and (2.16), respectively. They considered the following equations for the ternary kinematic viscosity and kinematic viscosity of the mixture:

$$v_{ijk} = \frac{hN_0}{M_{ijk}}\,e^{(\Delta G_{ijk}/RT)} \tag{2.25}$$

$$v_m = \frac{hN_0}{M}\,e^{(\Delta G_m/RT)} \tag{2.26}$$

$$M_{ijk} = (M_i + M_j + M_k)/3 \tag{2.27}$$

$$M = \sum_{i}^{n} x_i M_i \tag{2.28}$$

In order to eliminate the energy of activation terms, the logarithms on the kinematic viscosities equations were taken. Finally, a generalized three-body interaction model for the multi-component systems was obtained as follows:

$$\ln v_m = \sum_{i=1}^{n} x_i^3 \ln(v_i M_i) + 3\sum_{i=1}^{n}\sum_{j=1}^{n} x_i^2\,x_j \ln\left(v_{ij} M_{ij}\right) + 6\sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n} x_i^2 x_j x_k \ln\left(v_{ijk} M_{ijk}\right) - \ln(M) \tag{2.29}$$

The resulting model consists of binary and ternary interaction parameters and can be used as a correlative model for the multi-component mixtures. Nhaesi and Asfour (2000a) converted the correlative model into a predictive model by benefiting from the technique developed and reported by Asfour *et al.* (1991).

2.2.5. Conversion of the McAllister three-body and four-body models from correlative to predictive for *n*-alkane binary systems

Asfour *et al.* (1991) pointed out that the McAllister model's main deficiency is its correlative nature since it requires relatively extensive experimental database determine the values of the adjustable parameters. Since obtaining the required experimental data is both time-consuming and costly, it is important to convert the McAllister model into a predictive model. Asfour (1980) classified the systems into three categories: *n*-alkanes, regular solutions and associated mixtures. This enabled Dullien and Asfour (1985) and Asfour and Dullien (1986) to solve the prediction of molecular diffusion in liquid systems problem. Asfour *et al*. (1991) took a similar approach for the prediction of the viscosity of liquid mixtures. Asfour *et al*. (1991) started by employing their technique to binary *n*-alkane liquid systems. They used pure component viscoisities and molecular parameters in order to determine the values of the adjustable parameters in the McAllister model. They were met with enormous success and obtained excellent results. The average absolute deviation they obtained was less than 1%. The novel method that Asfour *et al.* (1991) proposed can be summarized as follows: (i) fitting data to Equation (2.19), (ii) assuming that the binary interaction parameter, v_{12}, is proportional to the $({v_1}^2 v_2)^{1/3}$, which was called the lumped parameter. Asfour *et al.* (1991) provided a rationale for such an assumption (iii) They plotted the lumped parameter versus 1/T as shown in Figure (2.4). The plot of the lumped parameter versus the inverse of temperature gave horizontal straight lines. This indicated that the the lumped parameters were independent of temperature, (iv) They plotted the lumped parameter versus a function of the number of the carbon atoms of the components of the binary *n*-alkane mixture. The function is shown in Equation (2.30) as follows:

$$\frac{v_{12}}{(v_1^2 v_2)^{1/3}} = 1 + 0.044 \frac{(N_2 - N_1)^2}{(N_1^2 N_2)^{1/3}} \tag{2.30}$$

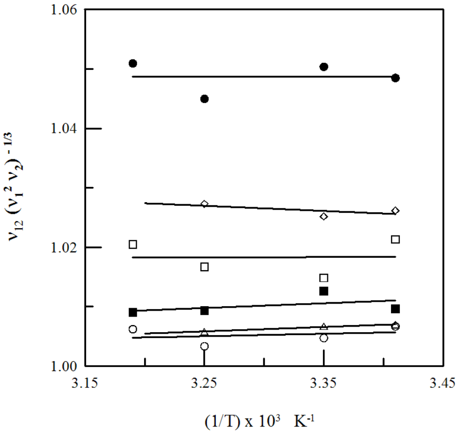


Figure 2.4. The lumped parameter's variation with (1/T) for binary *n*-alkane systems (Asfour *et al.* 1991).

Therefore, a new term was defined based on the relative difference of number carbon atoms, $\frac{(N_2-N_1)^2}{(N_1^2 N_2)^{1/3}}$, of two components constituting a mixture (v) A plot of the lumped parameter versus the difference in the numbers of the carbon atoms between the two components of the n-alkane mixture is shown in Figure (2.5), The least-squares method was employed to obtain the linear relationship between the lumped parameter and the difference between the number of carbon atoms function. The relationship is given by Equation (2.30). This enabled Asfour *et al.* (1991) to determine the value of the McAllister interaction parameter, v_{12}, from the pure component kinematic viscosities and the number of carbon atoms of constituent components in the binary *n*-alkane mixture.

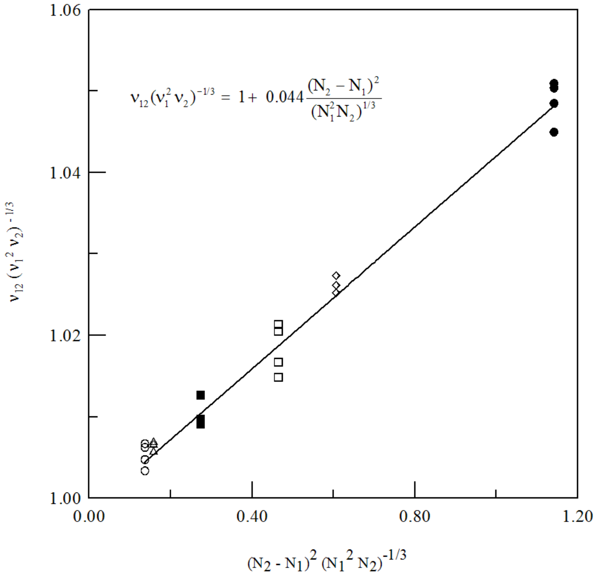


Figure 2.5. The lumped parameter variation for *n*-alkane systems based on the term as a function of the number of carbon atoms (Asfour *et al.* 1991)

In order to calculate the second binary parameter, v_{21}, Asfour *et al.* (1991) suggested using the relationship given by Equation (2.31), which they provided a proper rationale for,

$$v_{21} = v_{12}\left(\frac{v_2}{v_1}\right)^{1/3} \tag{2.31}$$

The set of data that was utilized in developing Equation (2.30) was not used in testing the model. The technique was highly satisfactory over the range of *n*-alkane systems test. They also tested the McAllister four-body interaction model using the same technique. Equation (2.30) was used to convert the correlative McAllister model into a predictive one.

$$\frac{v_{12}}{(v_1^2 v_2)^{1/3}} = 1 + 0.03\frac{(N_2-N_1)^2}{(N_1^2 N_2)^{1/3}} \tag{2.32}$$

In order to determine the binary interaction parameters of four body model, Equation (2.32) was obtained. Similarly, Equations (2.33) and (2.34) were developed,

$$v_{21} = v_{12}\left(\frac{v_2}{v_1}\right)^{1/4} \tag{2.33}$$

$$v_{2221} = v_{1122}\left(\frac{v_2}{v_1}\right)^{1/4} \tag{2.34}$$

As pointed earlier, the four-body McAllister model is applicable for the systems with a radii ratio of components over 1.5. Asfour *et al*. (1991) found that the four-body model can perform better when using it in the binary systems with over three carbon atom difference.

2.2.6. Conversion of the McAllister three-body model from correlative to predictive for binary regular systems

Nhaesi and Asfour (1998) extended the technique to make the model applicable to systems containing regular components. They introduced the *effective carbon number* [*ECN*] concept to account, in a similar manner, for the number of carbon atoms in *n*-alkane systems.. The kinematic viscosity of components at an absolute temperature of 308.15 was utilized to find the *ECN* parameter. As can be seen from Figure (2.6), plotting the logarithm of the kinematic viscosities of liquid *n*-alkanes versus their respective number of a carbon atoms gave a straight line. The equation of the straight line depicted in Figure (2.6) was reported by Nhaesi and Asfour (1998) as follows:

$$\ln v = -1.943 + (0.193 \times ECN) \tag{2.35}$$

Knowing the kinematic viscosity of the component in a regular solution at 308.15 K makes it possible to calculate its *ECN* with the help of Equation (2.35). The *ECN* can now be used for regular solution systems instead of the number of carbon atoms, *N*. in Equations (2.30) through (2.32).

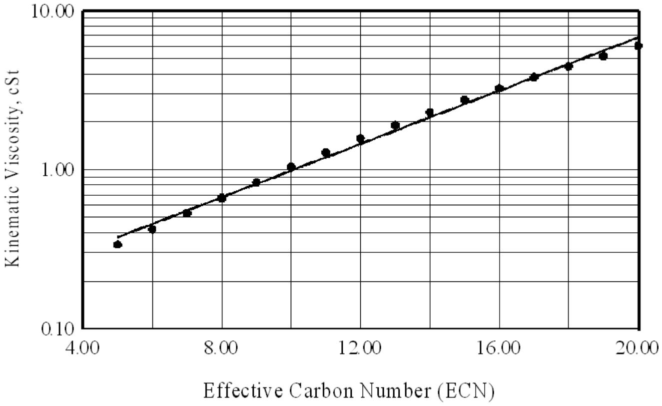


Figure 2.6. Experimental values of the kinematic viscosities of n-alkane systems at 308.15 K versus the effective carbon number (Nhaesi and Asfour, 1998).

In order to make the value of *ECN* utilizable for calculating the binary interaction parameter of systems containing regular components, Nhasi and Asfour (2000a) regressed the lumped parameter against the term, which was a function of *ECN.* They obtained the following equation:

$$\frac{v_{12}}{\left(v_1^2 v_2\right)^{1/3}} = 0.8735 + 0.0715\frac{(ECN_2 - ECN_1)^2}{\left(ECN_1^2 ECN_2\right)^{1/3}} \qquad (2.36)$$

2.2.7. Conversion of the generalized McAllister three-body model from correlative into predictive for multicomponent systems

Nhaesi and Asfour (2000a) converted the generalized, Equation (2.29), to a predictive model. Equation (2.29) contains two types of parameters; *viz.*, the binary interaction parameter, v_{ij}, and the ternary interaction parameter, v_{ijk}. Based on Sections 2.2.5 and 2.2.6, the binary parameters were calculated using equations relevant to each system type; *viz.*, *n*-alkanes and regular systems. Nhaesi and Asfour (2000a) used the binary predictive parameters in Equation (2.29) to find the best ternary parameter equation. They obtained the following equation for the calculation of the ternary interaction parameter:

$$\frac{v_{ijk}}{\left(v_i v_j v_k\right)^{1/3}} = 0.9637 + 0.0313\frac{(N_k - N_i)^2}{N_j} \qquad (2.37)$$

Subscripts i, j and k were defined as components in a different selection of components 1, 2 and 3 in order of their weights, respectively. Nhaesi and Asfour (2000a) indicated that the number of parameters depends on the number of constituent components. N_2 and N_3 are the numbers of binary and ternary parameters, respectively.

$$N_2 = \frac{n!}{(n-2)!} \tag{2.38}$$

$$N_3 = \frac{n!}{3!(n-3)!} \tag{2.39}$$

Where n is the number of constituent components of a liquid solutions.

2.2.8. The McAllister three-body *pseudo*-binary model

Wu and Asfour (1992) proposed a *pseudo*-binary model that results in decreasing the number of interaction parameters of the GCSP model resulting from the increase in the number of components. Nhaesi and Asfour (2000b) incorporated the *pseudo*-binary model into the McAllister three-body model. As can be seen from Equations (2.38) and (2.39), the number of different interactions increases as the number of components in a system increases. Wu and Asfour (1992) considered the multi-component system as a binary system with component one, defined as a and the *pseudo*-component b' which consists of components 2, 3, …, n. The following equations were employed for calculating the *pseudo*-binary interaction parameter:

$$\frac{v_{ab}'}{(v_a^2 v_b')^{1/3}} = 0.044\frac{(N_b' - N_a)^2}{(N_a^2 N_b)^{1/3}} + 1 \tag{2.40}$$

$$ECN_{b'} = \sum_{i=2}^{n} X_i ECN_i \tag{2.41}$$

$$Ln\, v_{2'} = \sum_{i=2}^{n} X_i \ln v_i \tag{2.42}$$

$$Ln\, M_{2'} = \sum_{i=2}^{n} X_i \ln M_i \tag{2.43}$$

$$X_i = \frac{x_i}{\sum_{i=2}^{n} x_i} \tag{2.44}$$

where ν_a and $\nu_b{}'$ are the kinematic viscosities of components a and *pseudo*-component b', respectively. The effective carbon number of pure component i and *pseudo*-component b' were denoted as ECN_i and $ECN_{b'}$, respectively. The mole fractions, x_i, must be normalized with the help of Equation (2.44) to the new normalized mole fraction, X_i. Besides, the molecular weight of the *pseudo*-binary component, $M_{2'}$, should be calculated for every point of the system based on the different composition of components.

2.2.9. The GC-UNIMOD model (Group Contribution Method)

Cao *et al.* (1992) used statistical thermodynamics and the Eyring rate theory to develop a new model. They considered the probability of different molecules' placement in the hypothetical lattice based on the difference of sizes and molecular interactions between two molecules of systems to develop their model. The local composition concept was used to determine both the effects of mixture components' sizes and forces on the viscosity property. The UNIFAC model is a famous local composition model that is still used as a powerful predictive model to predict systems' activity coefficient. On the basis of the Cao *et al.* (1992) treatment, the kinematic viscosity of a liquid mixture is calculated by the following equation:

$$\ell n\left(\nu M\right)=\sum_{i=1}^{n} x_i\, \ell n\left(\nu_i M_i\right)-\sum_{i=1}^{n} q_i n_i x_i \sum_{j=1}^{n} \theta_{ji} \ell n\, \tau_{ji} \tag{2.45}$$

where M is the molecular weight of the liquid mixture. M_i and x_i are the molecular weight and composition of component i, respectively. Based on the Abrams and Prausnitz (1975), q is structural parameters called pure component area parameter. Parameter n_i is also defined as the proportionality constant of segment i, which is determined by the following relation:

$$\ln(n_i) = \sum_{j=0} A_j T^j \tag{2.46}$$

where the A_j set as the adjustable parameters. In addition, θ_{ij} is the local composition area fraction calculated by:

$$\theta_{ij} = \frac{\theta_i \tau_{ji}}{\sum_{l=1}^{n} \theta_{li} \tau_{li}} \tag{2.47}$$

where the area fraction, θ_i, and intermolecular interaction, τ_{ij}, are,

$$\theta_i = \frac{x_i q_i}{\sum_{l=1}^{n} x_j q_j} \tag{2.48}$$

$$\tau_{ij}=\exp\left(-5\,\frac{U_{ji}-U_{ii}}{RT}\right) \tag{2.49}$$

The U_{ji} and U_{ii} are the potential energy interaction between j ←→ i and i ←→ i, respectively. The adjustable parameters of the model indicate the correlative feature of the model. Cao *et al.* (1993a) proposed the UNIMOD model based on the thermodynamic properties of the components, like the activity coefficient where experimental activity coefficient data are readily available in the literature. The model calculates the adjustable parameter based on both viscosity or activity coefficient data using a correlative approach. The proposed UNIMOD equations are as follows:

$$\ln(vM) = \sum_{i=1}^{n} \phi_i \ln(v_i M_i) + 2\sum_{i=1}^{n} \phi_i \ln\left(\frac{x_i}{\phi_i}\right) - \sum_{i=1}^{n} \frac{q_i n_i \phi_i}{r_i} \sum_{j=1}^{n} \theta_{ji} \ln(\tau_{ji}) \tag{2.50}$$

$$\phi_i = \frac{x_i r_i}{\sum_{l=1}^{n} x_j r_j} \tag{2.51}$$

M_i is the molecular weight, and r_i is the structural parameter called volume parameter or number of segments in a molecule *i,* and ϕ_i is the segment fraction of component *i,* which is determined by Equation (2.51).

Cao *et al.* (1993b) developed their model on the basis of the intermolecular forces of binary group contribution. The model was named the group contribution UNIMOD (GC-UNIMOD) model. The model's group contribution parameters were extracted from the UNIFAC activity coefficient model, which is widely applied for the prediction of the phase behaviour of vapour-liquid equilibria (VLE) systems. The model consists of two parts; the first part is known as the combinatorial part whereas the second is known as the residual part. The parameters and interactions are commonly defined by the residual part in local composition (LC) models. The following equations are the combinatorial and residual parts of the GC-UNIMOD model:

$$\xi_i^{comb} = \phi_\mathrm{i} \, \ell\mathrm{n}\left(\nu_\mathrm{i} \frac{\mathrm{M_i}}{\mathrm{M}} \right) + 2\,\phi_\mathrm{i} \, \ell\mathrm{n}\left(\frac{\mathrm{x_i}}{\phi_\mathrm{i}} \right) \tag{2.52}$$

Herein, ν_i is the viscosity of pure component at the specific temperature.

$$\xi_i = \sum\nolimits_{all\ groups\ k} \nu_k^{(i)} \left[\Xi_{\mathrm{ki}} - \Xi_{ki}^{(i)} \right] \tag{2.53}$$

where $\Xi_{ki}^{(i)}$ is the residual viscosity of group k for component i in the mixture, and $\mathrm{v}_k^{(i)}$ is the number of groups k in the component i of the solution. The Ξ_{ki} is calculated by,

$$\Xi_{mi} = -\frac{Q_m}{R_m} N_{mi}^{vis} \, \phi_i \sum_{all\ groups\ k} \theta_{km} \, \ell n\left(\Psi_{km}\right) \tag{2.54}$$

The Q_k and R_k are the geometrical parameter of group *k* used to calculate the structural parameter of q_i and r_i, respectively. Ψ_{km} represents the model's binary interaction parameter between-group *k* and *m* in the model and is denoted as the viscosity parameter of group *k* in component *i,* which is dependent on structural parameters r and q. The following equations are used to calculate the parameters in Equation (2.54):

$$Q_k = \frac{A_{wk}}{2.5 \times 10^9} \tag{2.55}$$

$$R_k = \frac{V_{wk}}{15.17} \tag{2.56}$$

$$N_{ki}^{vis} = Q_k \left(\frac{q_i - r_i}{2} - \frac{1 - r_i}{z} \right) \tag{2.57}$$

$$\Psi_{km} = exp\left(-\frac{a_{km}}{T} \right) \tag{2.58}$$

$$q_i = \sum_{(all\ group\ k)} v_k^{(i)} Q_k \tag{2.59}$$

$$r_i = \sum_{(all\ group\ k)} v_k^{(i)} R_k \tag{2.60}$$

where the A_{wk} and V_{wk} are the van der Waals' area and volume of group *k,* respectively. The parameter a_{km} is denoted as the interaction energy parameter of groups *k* and *m*.

CHAPTER 3

CONVERSION OF THE GENERALIZED MCALLISTER FOUR-BODY COLLISION MODEL FROM CORRELATIVE INTO A PREDICTIVE MODEL

3.1. General

Nhaesi and Asfour (2000a) published a generalized three-body interaction McAllister predictive model for multi-component regular liquid mixtures. They tested their model using an extensive database of regular liquid systems. The model was successful in predicting the viscosities of a large number of systems. However, there were cases where the large difference in the size between some components of systems, where the predictions were not that successful. This represented the motive for the present author to develop a four-body interaction predictive McAllister model to deal with such cases. Consequently, the objectives of the present work include: (i) the development of a generalized McAllister four-body model for multi-component liquid mixtures, (ii) development of Asfour *et al.* (1991) technique for the determination of each type of the model parameters, (iii) validating the generalized model and techniques used for the prediction of parameters, (iv) incorporating the *pseudo*-binary into the generalized McAllister four-body model to reduce the number of parameters involved, (v) comparing the four-body McAllister model and *pseudo*-binary model predictions with three other predictive methods; *viz.*, the GC-UNIMOD, the McAllister three-body and the *pseudo*-binary McAllister three-body models.

3.2. Modelling Details

3.2.1. Development of the generalized McAllister model for multi-component liquid mixtures based on four-body molecules configuration

McAllister proposed his model for the calculation of the dependence of viscosity on the composition of liquid binary mixtures. The McAllister model was developed on the basis of the Eyring reaction rate theory,

$$v = \frac{hN_0}{M} e^{\Delta G/RT} \tag{3.1}$$

where R is the universal gas constant. Equation (3.1) is utilized to develop a viscosity model for a multi-component mixture of n-components of type 1, 2, …, and n. Theoretically, as long as a molecule of type 1 passes the molecular energy impediment to the vacant area, interaction with another type 1 molecule, a type 2 molecule or a dual interaction with both cases could be possible. This interaction can be assumed on the basis of four neighboring molecules in planar geometry, which is called four-body interactions. According to McAllister, this assumption is valid for the cases where the difference in molecular sizes of the types of molecules is relatively high. For the four-body interaction model, there are many possible types of intermolecular interactions. It was assumed that the mole fraction of mixtures' components is only contributed to the probability of occurrence of different types of interactions.

As a result, the energy of activation should be expressed as follows:

$$\Delta G_{mix} = \sum_{i=1}^{n} x_i^4 \Delta G_i + 4 \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} x_i^3 x_j \Delta G_{iij} + 3 \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} x_i^2 x_j^2 \Delta G_{ij} + 6 \sum_{\substack{i=1 \\ i \neq j \neq k}}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} x_i^2 x_j x_k \Delta G_{ijk} + \sum_{\substack{i=1 \\ i \neq j \neq k \neq l}}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} \sum_{l=1}^{n} x_i x_j x_k x_l \Delta G_{ijkl} \tag{3.2}$$

Three additional assumptions were made in developing the equation. These are:

$$\Delta G_{ijji} = \Delta G_{ijij} = \Delta G_{ij} \text{ (binary Type 1)} \tag{3.3}$$

$$\Delta G_{iiij} = \Delta G_{iiji} = \Delta G_{ijii} = \Delta G_{jiii} = \Delta G_{iij} \text{ (binary Type 2)} \tag{3.4}$$

$$\Delta G_{iijk} = \Delta G_{ijik} = \Delta G_{ijki} = \Delta G_{jiki} = \Delta G_{iikj} = \Delta G_{ijk} \text{ (ternary)} \tag{3.5}$$

In order to proceed with the development of the model, the following terms were defined as follows:

The kinematic viscosity of the mixture is given by,

$$v_{mix} = \frac{hN_0}{M_{mix}} e^{\Delta G_{mix}/RT} \tag{3.6}$$

where

$$M_{mix} = \sum_{i=1}^{n} x_i M_i \tag{3.7}$$

For pure component i,

$$v_i = \frac{hN_0}{M_i} e^{\Delta G_i/RT} \tag{3.8}$$

For the binary interaction type 1,

$$v_{ij}{}^{I} = \frac{hN_0}{M_{ij}{}^{I}} e^{\Delta G_{ij}{}^{I}/RT} \tag{3.9}$$

where,

$$M_{ij}{}^{I} = \frac{M_i + M_j}{2} \tag{3.10}$$

For the binary interaction of type 2,

$$v_{ij}{}^{II} = \frac{hN_0}{M_{ij}{}^{II}} e^{\Delta G_{ij}{}^{II}/RT} \tag{3.11}$$

where,

$$M_{ij}{}^{II} = \frac{3M_i + M_j}{4} \tag{3.12}$$

The ternary interaction parameter is defined as follows:

$$v_{ijk} = \frac{hN_0}{M_{ijk}} e^{\Delta G_{ijk}/RT} \tag{3.13}$$

where

$$M_{ijk} = \frac{2M_i + M_j + M_k}{4} \tag{3.14}$$

The quaternary interaction parameter is expressed as follows:

$$v_{ijkl} = \frac{hN_0}{M_{ijkl}} e^{\Delta G_{ijkl}/RT} \tag{3.15}$$

where

$$M_{ijkl} = \frac{M_i + M_j + M_k + M_l}{4} \tag{3.16}$$

Taking the logarithms of Equations (3.6), (3.8), (3.9), (3.11) and (3.13) and substituting into Equation (3.2) to eliminate the free energy of activation, the following McAllister's four-body interaction model for the n-component liquid system is obtained:

$$ln v_{mix} = \sum_{i=1}^{n} \sum_{\substack{j=1 \\ i \neq j \neq k \neq l}}^{n} \sum_{k=1}^{n} \sum_{l=1}^{n} x_i x_j x_k x_l \ln\left(v_{ijkl} \frac{M_{ijkl}}{M_1}\right) + 6 \sum_{i=1}^{n} \sum_{\substack{j=1 \\ i \neq j \neq k}}^{n} \sum_{k=1}^{n} x_i^2 x_j x_k \ln\left(v_{ijk} \frac{M_{ijk}}{M_1}\right) + \cdots$$

$$3 \sum_{i=1}^{n} \sum_{\substack{j=1 \\ i \neq j}}^{n} x_i^2 x_j^2 \ln\left(v_{ij}^{I} \frac{{M_{ij}}^{I}}{M_1}\right) + 4 \sum_{i=1}^{n} \sum_{\substack{j=1 \\ i \neq j}}^{n} x_i^3 x_j \ln\left(v_{ij}^{II} \frac{{M_{ij}}^{II}}{M_1}\right) + \sum_{i=1}^{n} \sum_{\substack{j=1 \\ i \neq j}}^{n} x_i^4 \ln\left(v_i \frac{M_i}{M_1}\right) - \ln\left(\frac{M_{mix}}{M_1}\right)$$

(3.17)

Equation (3.17) is a generalized McAllister four-body interaction model. Due to the four-body interaction model's assumption, three categories of interaction parameters are involved; *viz*., binary type 1 and 2, ternary and quaternary parameters. The numbers of the binary, ternary and quaternary interaction parameters depend on the number of components. The number of binary interaction parameter type 1, N_1^I, in an n-component system is given by,

$$N_1^I = \frac{n!}{2(n-2)!} \tag{3.18}$$

whereas the number of binary interaction type 2 is equal to,

$$N_2^{II} = \frac{n!}{(n-2)!} \tag{3.19}$$

The number of the ternary interaction parameters can be calculated with the help of the equation,

$$N_3 = \frac{n!}{2(n-3)!} \tag{3.20}$$

Equation (3.21) is used for calculating the number of the quaternary interaction parameter in an n-component mixture,

$$N_4 = \frac{n!}{24(n-4)!} \tag{3.21}$$

where n is the number of components in the systems. In the present study, new equations based on the Asfour *et al.* (1991) technique to generalize the McAllister four-body model to be applicable to regular liquid mixtures. The combination of proposed techniques results in converting the McAllister four-body model to a predictive model for the multi-component mixtures.

3.2.2. Development of a technique for predicting the McAllister four-body binary parameters

With regards to extending the Asfour *et al.* (1991) approach for the regular solutions, one needs to know the number of carbon atoms in each component. This can be done in the case of *n*-alkane solutions. However, for non-*n*-alkane liquid mixtures, one cannot use the number of carbon atoms as in the case of *n*-alkane mixtures. Therefore, Nhaesi and Asfour (1998) introduced the concept of the *Effective Carbon Numbers* (*ECN*) to address this problem as was explained earlier in Chapter 2, Subsection 2.2.6. In order to determine the numerical value of *ECN* for any regular component, one needs to know the kinematic viscosity of that component at 308.15 K and use Equation (2.35) to calculate its *ECN.* For the case of cyclic component, e.g.,cyclohexane and cyclooctane, according to their structure and size, Al-Gherwi suggested multiplying the value obtained from Equation (2.35) by 0.75 since Equation (2.35) was found to overpredict the *ECN* values for cyclic compounds because of unusal structure, Experimental kinematic viscosity data gathered from the literature in the temperature range 293.15 through 313.15 K were are utilized to determine the dimensionless lumped parameter, , $\frac{v^I_{ij}}{(v_i v_j)^{1/2}}$, for the sake of binary interaction type 1 calculations. Figure (3.1) shows that the dimensionless binary lumped parameter is independent of the inverse of temperature. The temperature parameter is not significant to be used in this model to predict the value of the interaction paramters.

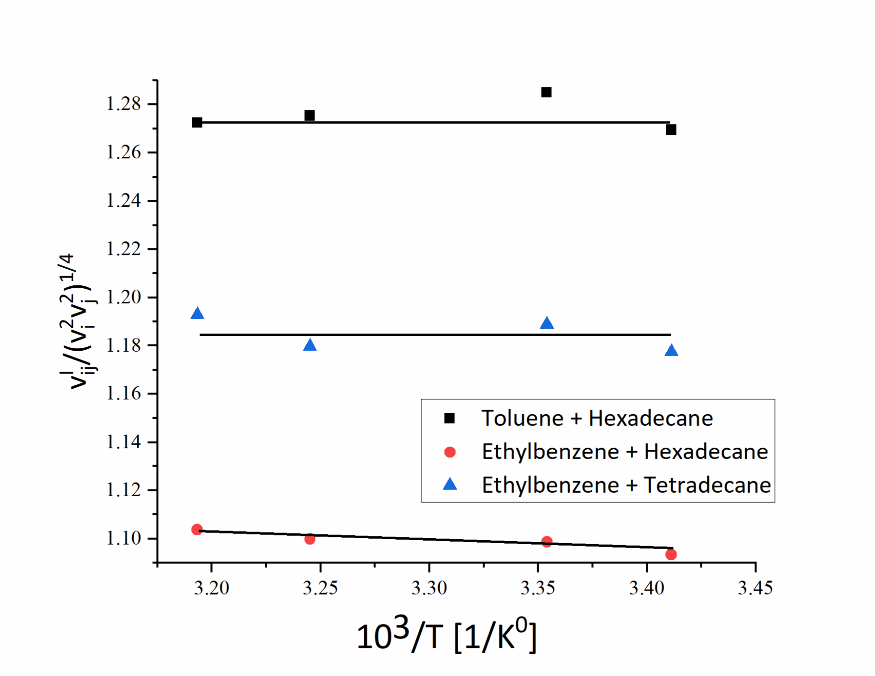


Figure 3.1. Variation of the binary type 1lumped parameter based on 1 / T (1/K) in three different regular systems, which are obtained from Nhaesi and Asfour (2000a)

Therefore, Figure (3.2) is similar to the earlier work of Nhasi and Asfour (2000a) but it is for the four-body interaction model. The dimensionless lumped parameter $\frac{v^I_{ij}}{(v_i v_j)^{1/2}}$ is plotted against $\frac{(N_j - N_i)^2}{(N_i N_j)^{1/2}}$. In Figure (3.2), where N_a and N_b are the effective carbon numbers of the first and second components, respectively. It gives a straight line shown in Figure (3.2).

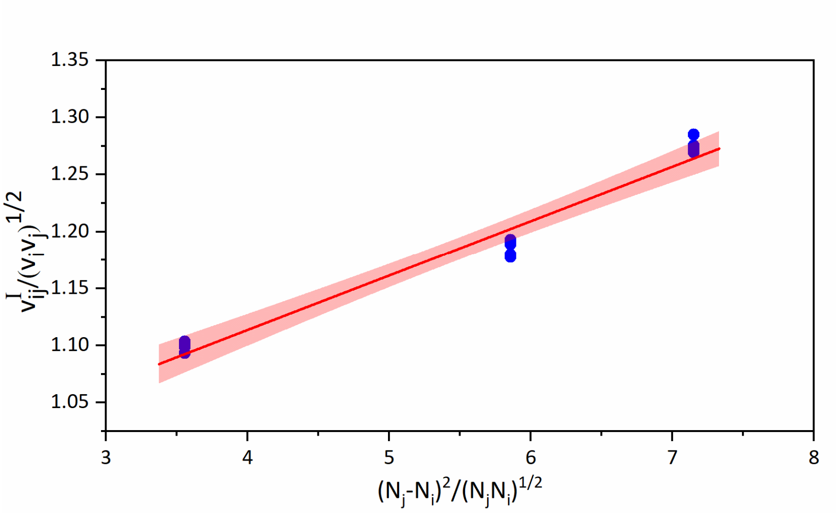


Figure 3.2 Variation of the binary type 1 lumped parameter based on the variation with $\frac{(N_j-N_i)^2}{(N_iN_j)^{1/2}}$.

The following equation is obtained by the Least-Squares method:

$$\frac{v^I_{ij}}{(v_iv_j)^{1/2}} = 0.0477\frac{(N_j-N_i)^2}{(N_iN_j)^{1/2}} + 0.9227 \tag{3.22}$$

In order to calculate type 2 binary interactions, v^{II}_{ab} and v^{II}_{ba}, the proportional technique was employed. Therefore, type 2 binary interaction can be calculated on the basis of the type 1 binary interaction.

$$v^{II}_{ij} = v^I_{ij}(\frac{v_i}{v_j})^{1/4} \tag{3.23}$$

$$v^{II}_{ji} = v^I_{ij}(\frac{v_j}{v_i})^{1/4} \tag{3.24}$$

For the binary 1-Alkanol systems, Hussein (2011) used the carbon number of 1-alkanols for calculating the binary interaction parameter equation of the McAllister three-body model. Therefore, for a better comparison, the type 1 binary interaction parameter equation reported by Asfour *et al.*(1991) is utilized for systems containing 1-alkanols. Equation (3.25) shows the old version of binary interaction equation type 1, which can be utilized for 1-alkanol systems in the McAllister four-body model,

$$\frac{v_{ij}^{I}}{(v_i v_j)^{1/2}} = 0.03\frac{(N_j - N_i)^2}{(N_i N_j)^{1/2}} + 1 \qquad (3.25)$$

where N is the number of carbon atoms in components *i* and *j*. For the validation of this technique, binary experimental data are compiled at different temperatures. The percentage absolute average deviation, defined by Equation (3.26) is used here to evaluate the model,

$$AAD\% = \frac{1}{n}\sum_{i=1}^{n}\frac{\left|v_i^{exp} - v_i^{cal}\right|}{v_i^{exp}} \qquad (3.26)$$

The results of comparison of the three predictive models are reported in Table 3.1.

3.2.3. Development of a technique for predicting the McAllister four-body ternary parameters

An extensive literature survey indicated that the McAllister four-body model was not used as a multi-component predictive model. In Equation (3.17) for the ternary systems, the value of ternary parameters, v_{ijk}, are required for predicting viscosities. For calculating the ternary parameters, expressed by Equations (3.23), (3.24) and (3.25), which are applied to calculate all binary interactions, the dimensionless lumped parameter, $\frac{v_{ijk}}{(v_i^2 v_j v_k)^{1/4}}$, should be calculated. Experimental kinematic viscosity data compiled from the literature (Nhaesi, 1998) over the temperature range 293 through -313 K were used to calculate the dimensionless ternary lumped parameter. Figure (3.3), again, shows that the lumped parameter is independent of temperature.

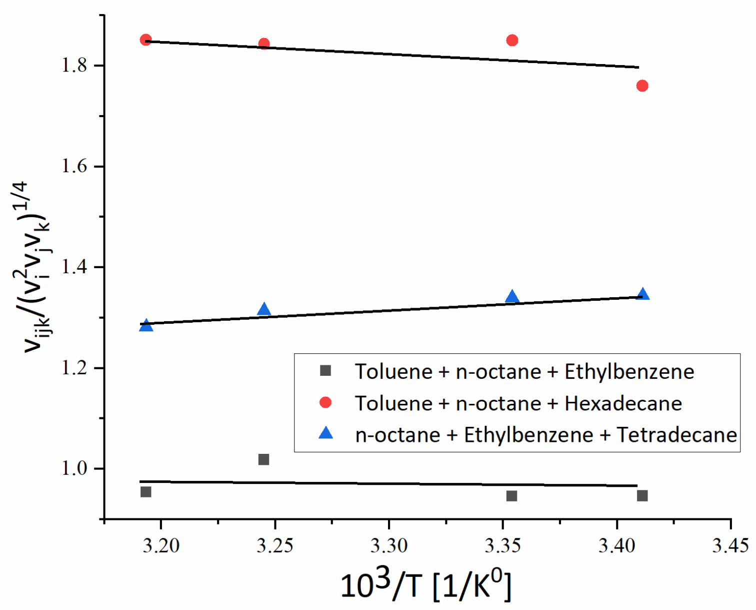


Figure 3.3. Variation of ternary lump parameter based on 1/T in three different regular systems, data given from literature (Nhaesi, 1998)

The scatter plot of $\frac{v_{ijk}}{(v_i^2 v_j v_k)^{1/4}}$ against $\frac{(N_i - N_j)^2}{N_k}$ where N_i, N_j and N_k are the effective carbon numbers of components *i, j* and *k*, respectively, gives a straight-line as depicted in Figure (3.4).

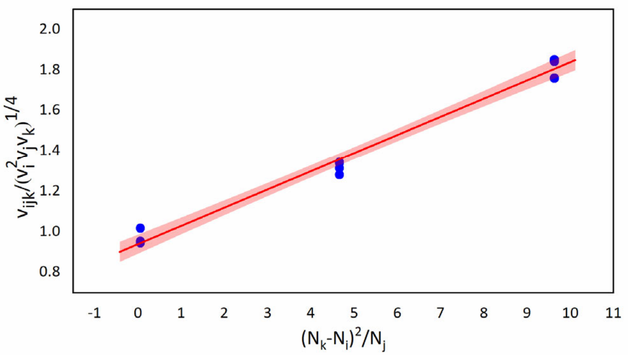


Figure 3.4. Variation of the ternary lumped parameter based on the variation of $\frac{(\boldsymbol{N_k} - \boldsymbol{N_i})^2}{\boldsymbol{N_j}}$.

The following equation, Equation (3.27), results from fitting data to obtain the ternary interaction parameter of 4-body interaction:

$$\frac{v_{ijk}}{(v_i^2 v_j v_k)^{1/4}} = 0.09\frac{(N_k - N_i)^2}{N_j} + 0.94 \tag{3.27}$$

where N_i, N_i and N_k refer to the higher effective carbon number of components i, j and k, respectively. For the validation of the ternary method, ternary experimental data are gathered.

It should be noted here that based on the number of components, the number of binary and ternary interaction parameters will change. In order to calculate other ternary interactions in the model, it is suggested to use Equation (3.27). However, by using the proportional equation as shown before in binary interaction type 2 calculations, no significant difference should not be observed in viscosity prediction.

3.2.4. Development of a technique for predicting the McAllister four-body quaternary parameters

The McAllister 4-body interaction model was extended on the basis of molecules in planar configuration for the system with more than four components; the quaternary interaction parameter is to be incorporated into the model. It is expected, in a similar manner to binary and ternary interaction parameters, quaternary ones are correlated to achieve a unique equation, but as the concept and base of the four-body-interaction model were fixed by the binary and ternary parameters, quaternary parameters are better to calculate based on the value of binary and ternary ones. Therefore, a proportional equation is proposed to be used to make the model simple. Equation (3.28) is given to calculate the four-body interaction quaternary interaction parameter of the model,

$$v_{ijkl} = v_{ijk}(\frac{v_l}{v_i})^{1/4} \tag{3.28}$$

Hence, using binary, ternary and quaternary interaction parameters, the McAllister four-body model converted to the general predictive model. It should be noted, again, that in Equations (3.18) through (3.21), the number of different types of parameters can be found. All obtained equations for predicting the interaction parameters should be applied to get consistent results. However, there is some modification in the aforement which will be discuused under results and discussion. For the validation of the quaternary method, quaternary and quinary data were used. The average absolute deviations for this model are reported and a comparison with the predictions of four other models; *viz.*, the GC-UNIMOD, the McAllister three-body interaction, the McAllister three-body *pseudo*-binary and the McAllister four-body *pseudo*-binary models is reported in Tables 3.4 and 3.5.

3.2.5. Incorporating the multi-component McAllister four-body interaction model into the *pseudo*-binary model

Extending the McAllister four-body interaction model to the multi-component mixtures would result in an increase in the number of interaction parameters since the number of components in the mixture increases. In order to resolve this issue, the *pseudo*-binary (Wu and Asfour, 1992) technique was applied to the McAllister four-body interaction model. They utilized this technique with the Generalized Corresponding States Principle (GCSP) model to address the deficiency of that model, where different selections of two reference fluids leads to different results. It should be noted that this technique was later employed by Nhaesi and Asfour (2000b) to reduce the number of the interaction parameters of the McAllister three-body interaction model, which led to satisfactory results. Wu and Asfour (1992) considered the *n*-component system as a binary mixture consisting of component one and a *pseudo*-component two, which included components 2, 3, 4, …, *n.* Therefore, this technique can be applied to mixtures with more than two components. The *pseudo*-binary model can simplify the modelling of systems containing more than three components.

In the case of the properties of *pseudo*-component, a mixing rule should be used. Equations (30) through (3.32) are incorporated into the McAllister model to convert it to a *pseudo*-binary McAllister model. In this case, the *effective carbon numbers*, kinematic viscosities and the molecular weights of the pure components, respectively are used. It should be pointed out here that for calculating each *pseudo*-component properties and the normalized mole fraction, X_i, must be used in order to obtain proper results.

$$(ECN)_{2'} = \sum_{i=2}^{n} X_i (ECN)_i \tag{3.29}$$

$$Ln\, v_{2'} = \sum_{i=2}^{n} X_i \ln v_i \tag{3.30}$$

$$Ln\, M_{2'} = \sum_{i=2}^{n} X_i \ln M_i \tag{3.31}$$

$$X_i = \frac{x_i}{\sum_{i=2}^{n} x_i} \tag{3.32}$$

where v_i, M_i and x_i are kinematic viscosity, molecular weight and mole-fraction of component *i* in a liquid mixture, respectively. These values should be used as the second component's properties in the *pseudo*-binary model of the McAllister four-body model. As it was shown by Equations (3.18) through (3.21), the number of different types of interaction parameters increases as the number of components increases. The *pseudo*-binary model can reduce the number of interaction parameters of different mixtures at two regardless the number of components in the mixture.

Equation (3.25) is used for calculating the binary type 1 parameter, as discussed earlier. After using Equation (3.25), the slope of the linear equation is changed to 0.044. Equation (3.33) performs better than Equation (3.25) where the slope is 0.03. Therefore, unlike Nhasi's suggestion (Nheasi, 1998), binary type1 relation, with slope 0.44 with the intercept 1 is utilized for the *pseudo*-binary McAllister four-body model of different systems.

$$\frac{v_{ij}^{I}}{(v_i v_j)^{1/2}} = 0.044 \frac{(N_j - N_i)^2}{(N_i N_j)^{1/2}} + 1 \tag{3.33}$$

In order to avoid the complexity of the model, this relation is used with all types of systems. However, for cases where larger *ECN* differences of three or more, it is suggested here to use binary interaction type 1 equation with a slope of 0.09 and intercept 1, which is determined by the use of the Nhaesi and Asfour (2000a) technique as discussed before.

$$\frac{v_{ij}^{I}}{(v_i v_j)^{1/2}} = 0.09\frac{(N_j - N_i)^2}{(N_i N_j)^{1/2}} + 1 \tag{3.34}$$

The main reason for this change is due to having a higher carbon effective number difference between component one and the *pseudo*-component. In other words, the ratio of the *pseudo*-component is much greater than the component one in the mixtures. Therefore, the former equations used in the general McAllister four-body model were not appropriate for the *pseudo*-binary McAllister model. For the validation of this technique, experimental data (binary, ternary, quaternary and quinary) are used. Again, the percent absolute average deviation, Equation (3.26) is used here as a criterion for evaluating the model. The results of testing are reported for comparison in Tables 3.1 through 3.5.

3.3. Result and Discussion

There are several types of liquid mixtures. In terms of thermodynamic properties, they show different behaviours relative to each other. Several issues can cause these differences. For example, molecular sizes and hydrogen bonding and the difference in their structures cause such differences. Therefore, it should be better to validate the model separately for each type of system. Herein, systems are divided into several categories: (i) 1-alkanol components, (ii) *n*-alkane components, (iii) regular components (iv) regular and 1-alkanol component nixtures. It should be noted here that some regular systems may include cyclic compounds. However, they are discussed in the following sections as they have more complicated behavior than other regular compounds.

3.3.1. Testing the predictive capability of the model in terms of binary systems

The average absolute deviations of the different regular binary systems are reported in Table 3.1. Since the techniques discussed earlier are only relevant to regular components, Equations (3.23) through (3.28) are only used for regular solution systems. The overall result of regular solutions shows that the McAllister four-body model has the least percent absolute average deviation compared with McAllister three-body and GC-UNIMOD models, which are 2.73, 2.83 and 5.64, respectively. As can be seen, the %AAD of the McAllister four-body model is better in almost all cases of regular mixture data with regular components compared to the three-body model. Only in two cases of systems containing cyclohexane and cyclooctane the results obtained using the four-body interaction model are not better than the predictions of the three-body interaction model. Careful analysis of the data clearly indicates that the McAllister four-body model improved the predictions compared with the predictions of the McAllister three-body interaction model when the molar volume ratio is more than 1.5. McAllister (1960) pointed-out that the correlative four-body model performed better than the three-body interaction model when the radii ratio of the molecules of the two components in a mixture is more than 1.5. Additionally, although the McAllister four-body interaction model results show better overall AAD% over the GC-UNIMOD model, in some cases, prediction of the kinematic viscosity of regular systems containing regular components by the GC-UNIMOD model shows the least deviation. This is clear for systems containing *m*-xylene, 1-chlorobutane, 2-chlorobutane and 2-methyl-1-choloropropane, indicating the exact values of physical parameters of such components for the GC-UNIMOD model.

According to the results reported in Table 3.2, the *AAD%* for the McAllister three-body interaction model related to 1-alkanol data is less than the McAllister four-body interaction and the GC-UNIMOD models. However, the McAllister four-body interaction model showed the best prediction in almost half of 1-alkanol binary data, whereas the GC-UNIMOD is least accurate in predicting the kinematic viscosity of the binary 1-alkanol systems.

Moreover, data for systems consisting of both 1-alkanol and regular components were utilized for the validation of the model. This category of the systems showed different behaviour compared to the two former types. According to Table 3.2, all models showed relatively unsatisfactory results in acse of systems containing 1-alkanol and regular components. The highest overall average absolute deviation can be found for the McAllister three-body interaction model. Even though the GC-UNIMOD gives relatively unsatisfactory results, however its deviation from experimental data is lower than the deviations of the McAllister three-body interaction model. Since this range of mixtures contains regular components, it is better to use, again, Equation (3.22) which uses the *ECN* in calculating the binary type 1 interaction parameter. However, the prediction would not be better than that of the three-body interaction model. Therefore, a new equation is proposed here to complement the McAllister four-body interactiom model. The new equation was developed on the basis of previously discussed techniques. Data on three systems at different temperatures were correlated (Kouris, 2002 and Feitosa *et al.* 2009),

$$\frac{v_{ij}^{I}}{(v_i v_j)^{1/2}} = 0.0244\frac{(N_j - N_i)^2}{(N_i N_j)^{1/2}} + 0.6715 \tag{3.35}$$

where *N* should be used as a number of carbon for the 1-alkanol components, but for the other regular components, it should be utilized as a carbon effective number. According to Table 2, the suggested equation for the systems, containing 1-alkanol and regular component, appropriately lowered the deviation from experimental values. According to Figure (3.5), the McAllister four-body interaction model is showing the best performance compared to the others whereas the GC-UNIMOD is the least accurate one for the prediction of the kinematic viscosity of tetrahydropyran and 1-buthanol mixture at 283.15 K. The *AAD's%* are 8.66, 25.23 and 14.85 for the McAllister four-body interaction, McAllister three-body interaction and the GC-UNIMOD models, respectively. Those results indicate improvement of the model in comparison with the McAllister three-body interaction model.

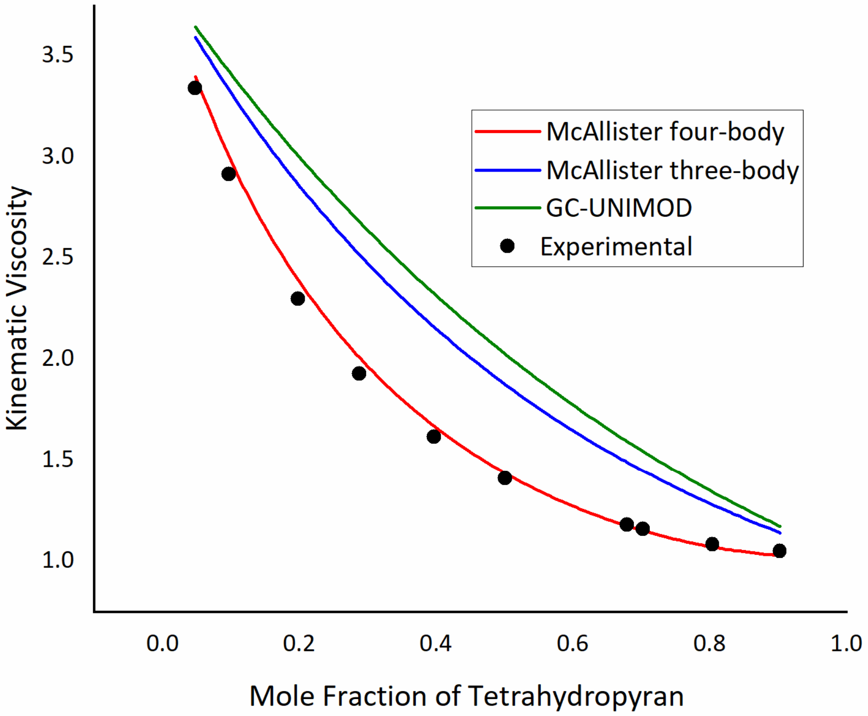


Figure 3.5. Prediction results of three different models for the binary system tetrahydropyran + 1-buthanol at 283 K, the experimental data is obtained from Valle *et al.* (2004),

It should be noted here that the binary interaction type 1 parameter is the most important parameter in the generalized multi-component McAllister model since the values of the other parameters in ternary, quaternary and quinary systems are determined on the basis of the binary parameters. Therefore, for the McAllister four-body interaction model, Equations (3.23), (3.26) and (3.36) can be used with the systems with regular components, 1-alkanol components and 1-alkanol + regular components, respectively.

3.3.2. **Testing the predictive capability of the model in terms of ternary systems**

The models were tested using four categories of experimental ternary data. Binary interaction parameters are determined in accordance with the last explanation on the basis of systems type.

For the sake of calculating the ternary interaction parameter, Equation (3.27) was utilized. The results are reported in Table 3.3.

For systems consisting of regular components, the proposed technique performed satisfactorily, where the *pseudo*-binary McAllister four-body interaction model showed a percent AAD of 3.02. According to Figure (3.6), the McAllister *pseudo*-binary four-body interaction, the *pseudo*-binary three-body interaction and the original McAllister four-body interaction models are showing the best conformity with the experimental points compared to the other models for the toluene-octane-hexadecane system at 298 K, respectively. The *pseudo*-binary McAllister three-body interaction and the GC-UNIMOD models showed the most deviation from experimental data among all models. On the basis of Figure (3.6), the GC-UNIMOD over-estimates the kinematic viscosity of the system for all points whereas other McAllister models under-estimate the value of kinematic viscosity.

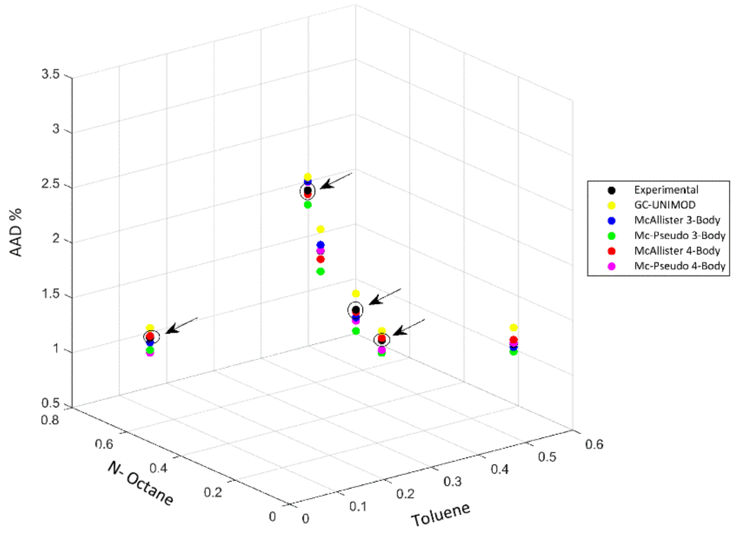


Figure 3.6. Prediction of the results of five different models for the ternary system (toluene + octane + hexadecane system at 298 K. The experimental data is obtained from Nhasi and Asfour (2000a).

According to Table 3.3, in terms of 1-alkanol components, the McAllister four-body interaction model did not show satisfactory performance compared to the McAllister three-body interaction model and the GC-UNIMOD. The overall %*AAD* in case of the McAllister four-body interaction model is reported to be about 4.2, which is higher than the other predictive models. The McAllister *pseudo*-binary four-body interaction model performed much better than the original McAllister four-body interaction model. The GC-UNIMOD model gave the best prediction results among the models, with a percent *AAD* of 1.42. Although the original McAllister three-body interaction model gave the best predictive capability for the 1-alkanol mixtures, with %*AAD* of 1.92. Applying the *pseudo*-binary technique shows a slight improvement in the prediction of kinematic viscosity of 1-alkanol mixtures, with a % AAD of 1.66. This agrees with conclusions made earlier by Nhasi and Asfour (2000b). Therefore, for both the cases of the McAllister models, three-body and four-body interactions, applying the *pseudo*-binary technique can be effective in obtaining better results in the 1-alkanols systems as concluded earlier by Nhasi and Asfour (2000b). Table 3.3 reports the results of testing different ternary systems.

Systems containing 1-alkanol and regular components are more challenging due to the different behaviour of these types of components, as was explained under the binary systems. The overall %*AAD* indicates the better predictive capability the McAllister four-body interaction model when compared with other models. This confirms that Equation (3.35) improves the performance of the model. The McAllister four-body interaction and the McAllister three-body interaction models predict the kinematic viscosity of such systems with %*AAD* of 6.83 and 8.22, respectively. It should be noted here the *pseudo*-binary model was not effective in improving the precision of both the four-body interaction and the three-body interaction McAllister models in case of systems containing 1-alkanols and regular components together. For systems containing just 1-alkanols or 1-alkanes, the *pseudo*-binary model was effective in improving the results. The main reason for this is the fact that for systems containing 1-alkanol with the regular component, more interaction parameters will be required to predict the complex behaviour of such systems.

3.3.3. Testing the predictive capability of the model in terms of quaternary and quinary systems

The generalized McAllister model was tested using quaternary and quinary liquid mixtures by employing the proportional quaternary interaction parameter equation. The models were tested using four categories of experimental data. The experimental data for the multi-component mixtures containing more than three components are rarely found in the literature. Asfour and co-workers reported work on quaternary and quinary liquid systems. The McAllister four-body interaction model was tested using such data. The testing results are reported in Tables 3.4 and 3.5 for the quaternary and quinary mixtures, respectively. The first category included regular components forming quaternary systems, where the McAllister three-body interaction model shows the best performance with % AAD of around 2.93. However, the McAllister four-body interaction model gives better %*AAD* over the GC-UNIMOD 3.46 versus 7.5, respectively. Results showed that the *pseudo*-binary model lowered predictive capability of the original McAllister models for the prediction of kinematic viscosity in regular quaternary systems. With regard to the second and third categories of data, *n*-alkane and 1-alkanol systems, the McAllister three-body interaction model shows the best performance with % AADs of 2.93 and 1.48, respectively. For the systems, 1-alkanol and regular components together, the results show better predictive capability of the developed McAllister four-body interaction model when compared with the other predictive models. This confirms the earlier results reported in the cases of the binary and ternary systems. Similar to the ternary systems, the *pseudo*- binary model was not effective in improving the predictive capability of the McAllister three-body and four-body interaction models. It can be concluded that due to the complex behaviour of this category of systems that more interaction parameters are needed to improve the predictive capability of the model.

For the quinary mixtures, just four systems at different temperatures were investigated. Therefore, in Table 3.5, the results are separated into three categories, and just the overall %*AADs* are reported to give an idea about the performance of the model. According to Table 3.5, the percent overall absolute average deviation shows that the McAllister four-body interaction model predicts the kinematic viscosity better than the McAllister three-body interaction model and the GC-UNIMOD models. The system: cyclohexane (1) + *p* - xylene (2) + chlorobenzene (3) + 1-propanol (4) + 1-octanol (5) confirms that the proposed four-body model can be used for this type of data since it shows almost 45 percent improvement over the McAllister three-body model. The GC-UNIMOD model showed a large deviation between the experimental data and the predicted kinematic viscosity values over the entire composition range. It should be pointed-out here that the *pseudo*-binary McAllister model was not capable of improving the performance of the original McAllister models. Results show that the %deviation from experimental kinematic viscosity increased to 6.37 and 4.31 for the McAllister three-body and four-body interaction models, respectively.

For the binary, ternary, quaternary and quinary regular systems, containing no 1-alkanol components, the McAllister four-body interaction model gives better predictions as long as the difference in the number of carbon atoms is three or more. This is similar to the observations reported by Nhasi and Asfour (2000a) for binary 1-alkane systems. Figure (3.7) is provided to show the predictive capability of the models for the prediction of kinematic viscosity in different categories of data.

In the case of correlation, it is expected to get very good results in every system with the McAllister four-body interaction model because there are more interaction parameters between four neighboring molecules. Also, the four-body interaction model is a quartic polynomial equation, whereas the three-body is cubic equation. These two main reasons prove the better capability of the McAllister four-body interaction model over the McAllister three-body interaction model. Some specific systems like acetone and methanol have different behaviors, and it is hard to correlate and predict the kinematic viscosity. This is simply because the acetone-methanol is a highly associated system, where hydrogen bonding and intermolecular forces play a major role. In the present work, the kinematic viscosity of the methanol-acetone system is modelled by three predictive models and the results have shown the better performance of GC-UNIMOD, the McAllister four-body interaction and three-body interaction models, respectively. This is in good agreement with the results reported earlier by McAllister (1960). However, it should be noted here that the present study is not aiming at predicting the viscosities of associated systems. To the best of the present author's knowledge, there is not to date any model that can successfully predict the viscosities of associated systems. All models tend to breakdown when data on associated systems are used.

The *pseudo*-binary McAllister models tend to perform satisfactorily for the case of n-alkanes and 1-alkanols systems whereas it was expected that more satisfactory results would be obtained by employing the original McAllister, three-body interaction and four-body interaction models.

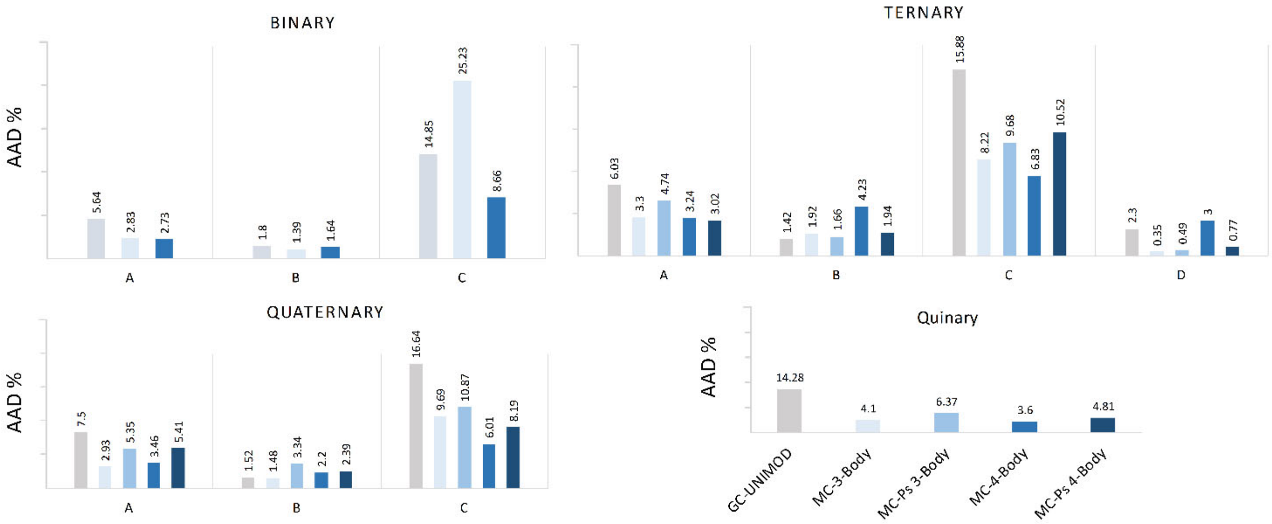


Figure 3.7. Comparison of the predictive capabilities of five models for binary, ternary, quaternary and quinary mixtures containing (a) Regular components (b) 1-alkanols, (c) 1-alkanol and regular components (d) *n*-alkanes.

3.4. Computer-Based Application for Predicting Viscosities using the McAllister Models

Asfour and co-workers efforts over the last four decades showed the great performance of the McAllister models. The McAllister models, 3-body and 4-body interactions show satisfactory results when compared with other models. These two types of models cannot be compared with each other as in systems with a molar-volume ratio of over 1.5, McAllister four-body model is expected to give better result.

Herein, we have provided a user-friendly application with a nice interface that the McAllister 3-body and 4-body interaction models are provided as a single model of McAllister. This toolbox is generated for use with the MATLAB software as a toolbox that can be easily installed. Figure (3.8) illustrates the algorithm flowchart of this application. According to Figure (3.9), the binary system of cyclohexane (1) + ethylbenzene (2) was predicted via this application, which validated the functionality of the toolbox. Also, this app is functional to predict the kinematic viscosity of multi-component systems.

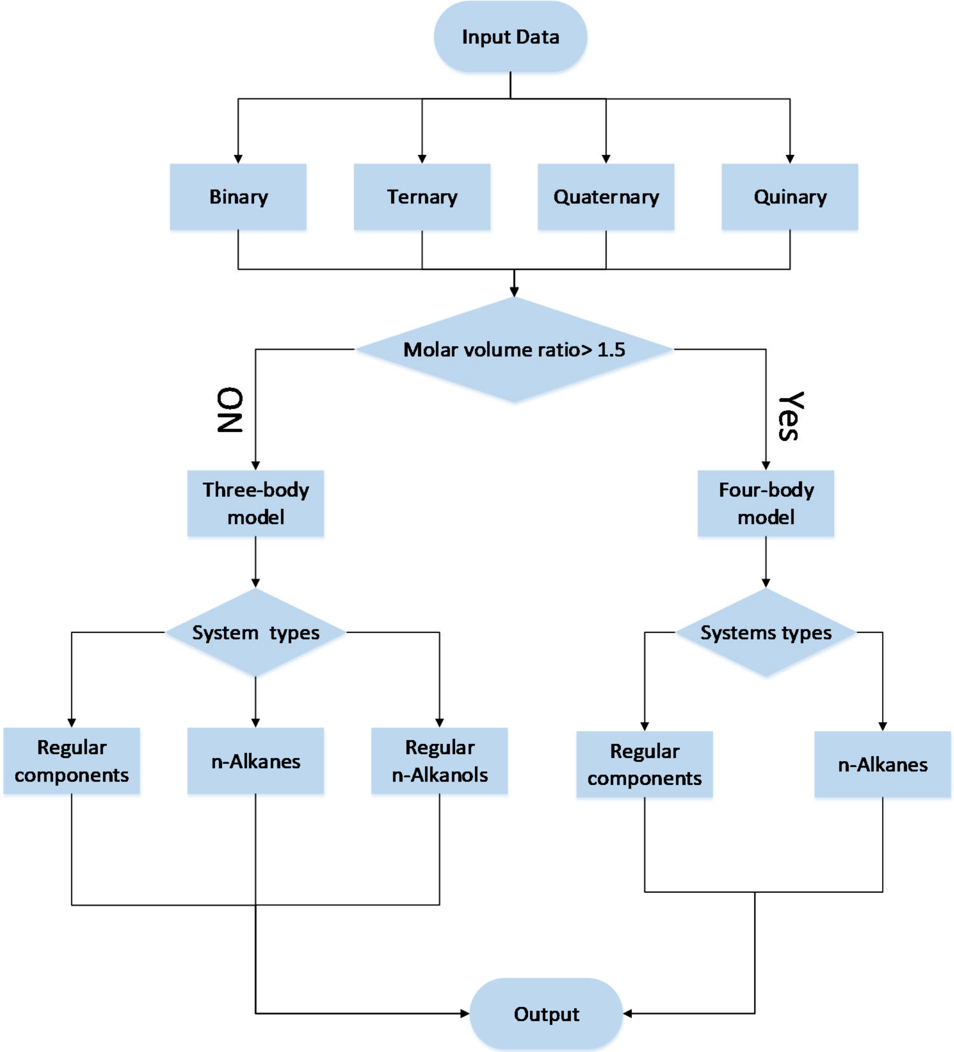
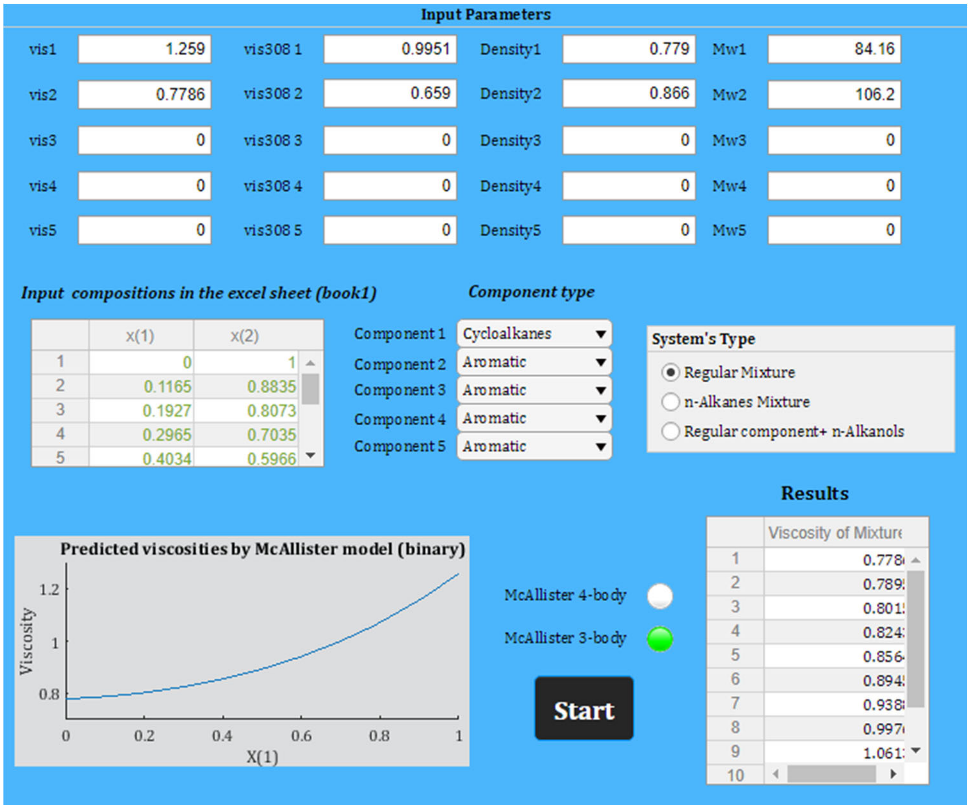


Figure 3.8. Algorithm of application, which selects the best model for predicting the kinematic viscosities of systems based on the system type and molar-volume ratio.

This application is provided with an excel sheet to support the users for inputting numerous composition data points of multi-component mixtures. The pure component properties are input into the application to run the model. The model will automatically select the best type of McAllister model on the basis of the molar volume ratio of the largest and smallest components in a mixture to predict the viscosities of the all given points.



Input Parameters

vis1	1.259	vis308 1	0.9951	Density1	0.779	Mw1	84.16
vis2	0.7786	vis308 2	0.659	Density2	0.866	Mw2	106.2
vis3	0	vis308 3	0	Density3	0	Mw3	0
vis4	0	vis308 4	0	Density4	0	Mw4	0
vis5	0	vis308 5	0	Density5	0	Mw5	0

Input compositions in the excel sheet (book1)

	x(1)	x(2)
1	0	1
2	0.1165	0.8835
3	0.1927	0.8073
4	0.2965	0.7035
5	0.4034	0.5966

Component type

Component 1	Cycloalkanes
Component 2	Aromatic
Component 3	Aromatic
Component 4	Aromatic
Component 5	Aromatic

System's Type

● Regular Mixture
○ n-Alkanes Mixture
○ Regular component+ n-Alkanols

Results

	Viscosity of Mixture
1	0.778
2	0.789
3	0.801
4	0.824
5	0.856
6	0.894
7	0.938
8	0.997
9	1.061
10	

McAllister 4-body ○
McAllister 3-body ●

Figure 3.9. Application control panel

Table 3.1. Results of testing the predictive capability of the two types of McAllister investigated models using the binary experimental viscosity data of regular mixtures.

Component 1	**Component 2**	**Np**	**T(K)**	**%AAD**		
				GC-UNIMOD	**3-Body**	**4-Body**
toluene	decane, dodecane, tetradecane Asfour *et al.* (1990), Vavanellos *et al*. (1991)	144	293- 313	6.05	1.39	0.65
toluene	ethylbenzene (Al-Ggherwi, 2005)	22	308-313	9.69	5.99	4.41
m-xylene	decane (Hamzehlouia and Asfour, 2012)	20	308, 313	0.54	1.75	0.67
p-xylene	chlorobenzene (Mohajerani, 2013)	22	293, 298	0.515	8.53	4.20
1-chlorobutane	2-methyltetrahydrofuran (Giner *et al.* 2003)	13	298	0.97	4.83	3.49
2-chlorobutane	2-methyltetrahydrofuran (Giner *et al*. 2003)	13	298	1.20	4.89	3.50
2-methyl-1-choloropropane	2-methyltetrahydrofuran (Giner *et al*. 2003)	26	298, 313	1.29	4.38	3.10
2-methyl-2-chloropropane	2-methyltetrahydrofuran (Giner *et al*. 2003)	13	298	1.95	3.65	2.38
tetrahydrofuran	benzene, toluene, fluorobenzene, chlorobenzene (Villares *et al.* 2004)	44	298	9.24	4.38	3.55
tetrahydropyran	benzene, toluene, fluorobenzene, chlorobenzene (Villares *et al.* 2004)	44	298	3.8	5.82	4.35
2-methyltetrahydrofuran	benzene, toluene, fluorobenzene, chlorobenzene (Villares *et al*. 2004)	44	298	3.6	3.66	3.13
2,5-dimethyltetrahydrofuran	benzene, toluene, fluorobenzene, chlorobenzene (Villares *et al*. 2004)	44	298	3.59	3.65	2.38
cyclohexane	*m*-xylene, cyclooctane, decane (Hamzehlouia and Asfour, 2012), ethylbenzene, toluene (Al-Gherwi, 2005), tetrahydrofuran (Gascón *et al*. 1999), chlorocyclohexane (Gascón *et al.*, 1999)	206	293- 313	7.33	2.1	3.18
cyclooctane	decane (Hamzehlouia and Asfour, 2012)	20	308, 313	9.83	1.89	3.21
chlorobenzene	decane (Hamzehlouia and Asfour, 2012)	20	308, 313	0.50	1.82	0.64
hexane	cyclohexane, ethylbenzene, toluene (Al-Gherwi, 2005)	66	293, 298	5.46	3.49	2.45
heptane	cyclohexane, ethylbenzene, toluene (Al-Gherwi, 2005)	132	293- 313	4.33	1.87	1.81
octane	cyclohexane, ethylbenzene, toluene (Al-Gherwi, 2005)	132	293- 313	3.81	2.14	1.44
Overall		1025	293-313	5.64	2.83	**2.73**

Table 3.2. Results of testing the predictive capability of the two types of McAllister investigated models using the binary experimental viscosity data of regular mixtures.

Component 1	**Component 2**	**Np**	**T (K)**	**%AAD**		
				GC-UNIMOD	**3B**	**4B**
n-Akanol + 1-Akanol						
methanol	ethanol (Dizechi and Marschall, 2002)	105	283- 323	1.47	0.69	0.60
methanol	1-propanol (Dizechi and Marschall, 2002)	14	303	8.32	1.71	1.28
ethanol	1-propanol (Dizechi and Marschall, 2002)	14	303	1.34	0.38	0.28
1-propanol	1-octanol (Mohajerani, 2013)	22	293, 298	1.66	1.23	1.13
1-propanol	1-heptanol (Hussein, 2019)	44	293- 313	1.21	1.25	1.04
1-propanol	1-nonanol (Hussein, 2019)	44	293- 313	1.255	1.55	2.44
1-propanol	1-undecanol (Hussein, 2019)	44	293- 313	4.24	3.06	4.49
1-pentanol	1-nonanol (Hussein, 2019)	44	293- 313	1.65	0.85	0.52
1-pentanol	1-undecanol (Hussein, 2019)	44	293- 313	2.39	1.67	1.82
1-heptanol	1-undecanol (Hussein, 2019)	44	293- 313	1.4	1.10	1.52
Overall		419	283- 323	1.80	1.39	**1.64**
Regular + 1-Akanol						
cyclohexane	1-propanol (Mohajerani, 2013), 2-buthanol (Gascón *et al.* 2000), octanol (Mohajerani, 2013), ethanol (Gascón et al, 2000)	63	293, 298	13.72	19.50	9.97
p-xylene	1-propanol, 1-octanol (Mohajerani, 2013)	44	293,298	24.22	23.98	17.95
chlorobenzene	1-propanol, 1-octanol (Mohajerani, 2013)	44	293,298	18.98	16.38	24.61
ethanol	hexane, octane, decane (Feitosa *et al.* 2009), methylethylketon, ethylacetate (Mussche and Verhoeye, 1975)	148	290- 298	8.30	42.5	5.11
methanol	aceton (Noda *et al*. 1982)	15	298	1.98	15.84	9.02
phenetole	1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol (Al-Jimaz *et al.* 2004)	264	293- 318	19.77	16.42	6.69
tetrahydropyran	1-buthanol (Vallés *et al.* 2004)	30	283- 313	22.20	16.22	4.66
Overall		608	283- 313	14.85	25.23	**8.66**

Table 3.3. Results of testing the predictive capability of the two types of McAllister investigated models using the ternary experimental viscosity data of various mixtures

Systems	Np	T(K)	%AAD				
			GC-UNIMOD	3B	*Pseudo*-3B	4B	*Pseudo*-4B
regular mixtures							
toluene (1) + octane (2) + tetradecane (3) (Nhaesi, 1998)	36	293- 313	6.92	1.95	2.19	1.15	1.6
toluene (1) + octane (2) + hexadecane (3) (Nhaesi, 1998)	36	293- 313	7.21	2.68	5.21	1.32	2.72
toluene (1) + ethylbenzene (2) + tetradecane (3) (Nhaesi, 1998)	36	293- 313	6.60	2.13	2.25	0.82	1.65
toluene (1) + tetradecane (2) + hexadecane (3) (Nhaesi, 1998)	36	293- 313	3.63	0.80	0.97	3.74	0.81
octane (1) + ethylbenzene (2) + tetradecane (3) (Nhaesi, 1998)	36	293- 313	6.18	1.41	1.42	*	1.65
octane (1) + ethylbenzene (2) + hexadecane (3) (Nhaesi, 1998)	36	293- 313	9.40	1.80	3.59	1.53	3.06
cyclohexane (1) + m-xylene (2) + cyclooctane (Hamzehlouia and Asfour, 2012)	20	308, 313	22.24	8.86	12	8.6	6.83
cyclohexane (1) + m-Xylene (2) + chlorobenzene (3) (Hamzehlouia and Asfour, 2012)	20	308, 313	6.22	4.37	6.13	3.01	2.13
cyclohexane (1) + m-Xylene (2) + decane (3) (Hamzehlouia and Asfour, 2012)	20	308, 313	8.43	0.99	5.87	2.61	1.095
cyclohexane (1) + cyclooctane (2) + chlorobenzene (3) (Hamzehlouia and Asfour, 2012)	20	308, 313	2.08	5.83	7.85	3.61	2.89
cyclohexane (1) + p-Xylene (2) + chlorobenzene (3) (Mohajerani, 2013)	20	293, 298	7.5	3.49	5.32	2.97	1.99
octane (1) + heptane (2) + ethylbenzene (3) (Elhadad, 2005)	26	293, 298	1.02	3.74	2.95	1.64	2.01
octane (1) + heptane (2) + toluene (3) (Elhadad, 2005)	26	293, 298	1.29	3.54	5.25	3.74	2.54
octane (1) + cyclohexane (2) + toluene (3) (Elhadad, 2005)	13	298	4.93	2.04	8.66	5.55	4.32
octane (1) + ethylbenzene (2) + toluene (3) (Elhadad, 2005)	26	293, 298	3.81	7.42	2.02	2.96	3.33
octane (1) + heptane (2) + cyclohexane (3) (Elhadad, 2005)	26	293, 298	0.37	2.00	6.56	3.21	2.81
heptane (1) + ethylbenzene (2) + cyclohexane (3) (Elhadad, 2005)	26	293, 298	4.36	3.15	7.64	4.30	3.3
octane (1) + ethylbenzene (2) + cyclohexane (3) (Elhadad, 2005)	26	293, 298	4.23	2.25	9.61	4.91	4.8

Table 3.3- Con’d.

ethylbenzene (1) + cyclohexane (2) + toluene (3) (Elhadad, 2005)	26	293, 298	8.04	3.03	8.37	4.97	4.68
cyclohexane (1) + tetrahydrofuran (2) + chlorocyclohexane (3) (Gascón *et al.* 1999)	96	298, 313	NAN	2.03	2.47	1.82	3.62
Overall	633	293-313	6.03	3.3	4.74	**3.24**	**3.02**
1-Akanol + 1-Akanol (Hussein, 2019)							
1-propanol (1) + 1-pentanol (2) + 1-heptanol (3)	20	308, 313	0.735	4.1	1.3	3.3	1.27
1-propanol (1) + 1-heptanol (2) + 1-nonanol (3)	40	293- 313	1.4675	0.70	1.33	3.79	1.63
1-propanol (1) + 1-pentanol (2) + 1-nonanol (3)	40	293- 313	2.445	2.50	1.53	2.53	1.71
1-propanol (1) + 1-heptanol (2) + 1-undecanol (3)	40	293- 313	2.255	1.26	1.66	5.14	1.68
1-propanol (1) + 1-pentanol (2) + 1-undecanol (3)	40	293- 313	1.45	2.68	4.09	3.47	5.61
1-pentanol (1) + 1-heptanol (2) + 1-nonanol (3)	40	293- 313	2.40	0.70	0.99	4.06	1.085
1-pentanol (1) + 1-nonanol (2) + 1-undecanol (3)	40	293- 313	1.26	2.50	0.62	4.61	0.98
1-pentanol (1) + 1-heptanol (2) + 1-undecanol (3)	40	293- 313	1.03	1.26	2.49	4.63	2.48
1-heptanol (1) + 1-nonanol (2) + 1-undecanol (3)	40	293- 313	0.56	2.68	0.73	6.10	0.675
Overall	340	293- 313	1.42	1.92	1.66	**4.23**	**1.94**
***n*-Alkane + *n*-Alkane** (Wu, 1992)							
C8 (1) + C11 (2) + C13 (3)	45	293- 313	2.03	0.21	0.32	1.93	0.63
C8 (1) + C11 (2) + C15 (3)	45	293- 313	3.49	0.49	0.65	2.78	0.70
C11 (1) + C13 (2) + C15 (3)	45	293- 313	0.90	0.27	0.12	3.97	0.17
C8 (1) + C13 (2) + C15 (3)	45	293- 313	3.59	0.55	1.1	3.01	1.80
C10 (1) + C13 (2) + C15 (3)	45	293- 313	1.48	0.21	0.24	3.45	0.52
Overall	225	293- 313	2.3	0.35	0.49	**3.00**	**0.77**
Regular + 1-Akanol (Mohajerani, 2013)							
cyclohexane (1) + p-Xylene (2) + 1-octanol (3)	20	293, 298	39.64	4.37	18.05	4.9	11.7
cyclohexane (1) + chlorobenzene (2) + 1-octanol (3)	20	293, 298	21.01	5.7	5.34	5.24	10.62
cyclohexane (1) + 1-propanol (2) + 1-octanol (3)	20	293, 298	6.575	6.95	5.29	5.9	7.83
p-xylene (1) + chlorobenzene (2) + 1-propanol (3)	20	293, 298	20.7	16.73	12.29	11.17	13.20
p-xylene (1) + chlorobenzene (2) + 1-octanol (3)	20	293, 298	10.545	8.30	4.2	5.49	6.66
p-xylene (1) + 1-propanol (2) + 1-Octanol (3)	20	293, 298	5.68	7.1	12.55	6.7	9.99
chlorobenzene (1) + 1-propanol (2) + 1-octanol (3)	20	293, 298	6.985	8.41	10.03	8.45	13.66
Overall	140	293, 298	15.88	8.22	9.68	**6.83**	**10.52**

* The correlated system in the model that was not used for calculating overall deviation.

Table 3.4. Results of testing the predictive capability of the two types of McAllister investigated models using the quaternary experimental viscosity data of various mixtures

Systems	Np	T(K)	%AAD				
regular mixtures			**GC-UNIMOD**	**3b**	***Pseudo*- 3b**	**4b**	***Pseudo*-4b**
toluene (1) + octane (2) + ethylbenzene (3) + tetradecane (4) (Nhaesi, 1998)	64	293- 313	7.37	2.48	2.03	1.63	1.96
toluene (1) + octane (2) + ethylbenzene (3) + hexadecane(4)	64	293- 313	8.94	2.15	4.86	2.13	4.96
toluene (1) + ethylbenzene (2) + tetradecane (3) + hexadecane(4)	64	293- 313	8.87	1.69	4.23	2.42	3.38
octane (1) + Ethylbenzene (2) + Tetradecane (3) + hexadecane(4)	64	293- 313	6.22	1.26	2.63	3.01	2.68
toluene (1) + octane(2) + tetradecane (3) + hexadecane(4)	64	293- 313	6.65	2.28	4.15	4.31	3.51
octane (1) + hexane (2) + ethylbenzene (3) + cyclohexane (4) (El-Hadad et al., 2015)	24	293, 298	9.41	2.24	7.76	4.45	7.70
octane (1) + hexane (2) + ethylbenzene (3) + toluene (4)	24	293, 298	3.60	3.59	2.30	2.28	2.39
octane(1) + heptane (2) + ethylbenzene (3) + cyclohexane (4)	24	293, 298	8.84	1.92	8.08	3.67	7.91
octane (1) + heptane (2) + ethylbenzene (3) + Toluene (4)	24	293, 298	5.12	7.49	3.84	4.39	4.89
octane (1) + heptane (2) + cyclohexane (3) + Toluene (4)	24	293, 298	4.92	3.90	7.83	4.07	7.93
heptane (1) + ethylbenzene (2) + cyclohexane(3) + toluene(4)	24	293, 298	7.42	2.76	8.79	4.26	8.66
octane (1) + ethylbenzene (2) + cyclohexane(3) + toluene(4)	24	293, 298	8.07	3.13	8.84	4.20	8.71
cyclohexane (1) + *m*-Xylene (2) + cyclooctane (3) + chlorobenzene (4) (Hamzehlouia and Asfour, 2013)	20	308, 313	11.91	4.50	8.43	6.45	9.08
cyclohexane (1) + *m*-Xylene (2) + cyclooctane (3) + decane (4)	20	308, 313	9.12	4.83	8.09	5.12	8.98
cyclohexane (1) + *m*-Xylene (2) + chlorobenzene (3) + decane (4)	20	308, 313	4.405	3.80	3.86	1.49	4.17
cyclohexane (1) + cyclooctane (2) + chlorobenzene (3) + decane (4)	20	308, 313	7.44	2.73	6.48	4.37	7.28
m-xylene (1) + cyclooctane (2) + chlorobenzene (3) + decane (4)	20	308, 313	9.23	3.83	7.73	5.52	8.47
Overall	588	293- 313	7.50	2.93	5.35	**3.46**	**5.41**
n-Akanol +1-Akanol (Hussein, 2019)							
1-propanol (1) + 1-pentanol (2) + 1-heptanol (3) + 1-nonanol (4)	40	293- 313	2.27	1.95	1.86	2.64	1.81
1-pentanol (1) + 1-heptanol (2) + 1-nonanol (3) + 1-undecanol (4)	40	293- 313	1.23	0.76	7.17	1.73	1.087
1-propanol (1) + 1-pentanol (2) + 1-nonanol (3) + 1-undecanol (4)	40	293- 313	1.74	0.99	1.86	2.56	3.07
1-propanol (1) + 1-pentanol (2) + 1-heptanol (3) + 1-undecanol (4)	40	293- 313	0.84	2.21	2.41	1.88	3.59
Overall	160	293- 313	1.52	1.48	3.34	**2.20**	**2.39**
Regular + 1-Alkanol (Mohajerani, 2013)							
cyclohexane (1) + *p*-xylene (2) + chlorobenzene (3) + 1-propanol (4)	20	293, 298	24.98	19.74	19.23	7.97	2.48
cyclohexane (1) + *p*-xylene (2) + chlorobenzene (3) + 1-octanol (4)	20	293, 298	14.88	3.81	8.11	5.20	7.85
cyclohexane (1) + *p*-xylene (2) + 1-propanol (3) + 1-octanol (4)	20	293, 298	25.00	8.83	10.44	5.39	8.62
cyclohexane(1) + chlorobenzene (2) + 1-propanol (3) + 1-octanol (4)	20	293, 298	8.86	7.64	7.59	5.54	12.27
p-xylene (1) + chlorobenzene (2) + 1-propanol (3) + 1-octanol (4)	20	293, 298	9.50	8.43	9.01	5.96	9.77
Overall	100	Overall	16.64	9.69	10.87	**6.01**	**8.19**

Table 3.5. Results of testing the predictive capability of the two types of McAllister investigated models using the quinary experimental viscosity data of various mixtures

Systems	N_p	T(K)	**AAD%**				
			GC-UNIMOD	3b	Pseudo- 3b	4b	Pseudo- 4b
toluene (1) + octan(2) + ethylbenzene(3) + tetradecane (4) + hexadecane (5) (Nhaesi, 1998)	15	293	10.56	3.43	4.52	3.68	3.75
toluene (1) + octan(2) + ethylbenzene(3) + tetradecane (4) + hexadecane (5) (Nhaesi, 1998)	15	298	10.78	1.63	4.36	1.63	3.73
toluene (1) + octan(2) + ethylbenzene(3) + tetradecane (4) + hexadecane (5) (Nhaesi, 1998)	15	308	7.11	3.19	4.22	2.15	3.95
toluene (1) + octan(2) + ethylbenzene(3) + tetradecane (4) + hexadecane (5) (Nhaesi, 1998)	15	313	7.46	2.01	2.89	1.42	3.02
octane (1) + hexane (2)+ ethylbenzene (3) + cyclohexane (4) + toluene (5) (El-Hadad *et al*, 2015)	14	293	6.93	1.22	5.73	3.31	5.96
octane (1) + hexane (2)+ ethylbenzene (3) + cyclohexane (4) + toluene (5) (El-Hadad *et al.* 2015)	14	298	6.27	0.901	5.35	3.01	5.55
cyclohexane (1) + *m*-xylene (2) + cyclooctane (3) + chlorobenzene (4) + decane (5) (Hamzehlouia and Asfour, 2013)	10	308	5.89	5.36	7.52	5.69	7.84
cyclohexane (1) + *m*-xylene (2) + cyclooctane (3) + chlorobenzene (4) + decane (5) (Hamzehlouia and Asfour, 2013)	10	313	6.11	4.96	7.2	5.46	7.51
cyclohexane (1) + *p*- xylene (2) + chlorobenzene (3) + 1-propanol (4) + 1-Octanol (5) (Mohajerani, 2013)	10	293	42.14	9.16	11.05	5.73	3.77
cyclohexane (1) + *p*- xylene (2) + chlorobenzene (3) + 1-propanol (4) + 1-octanol (5) (Mohajerani, 2013)	10	298	39.59	9.00	10.89	4.84	2.98
Overall	128	293-313	14.28	4.1	6.37	**3.60**	**4.81**

CHAPTER 4

A NEW METHOD FOR IMPROVING THE PREDICTION OF THE INTERACTION PARAMETERS OF THE *PSEUDO*-BINARY McALLISTER VISCOSITY MODELS

4.1. General

The dependence of viscosity on composition over the entire composition range is being investigated by researchers around the world.. Mathematical models are being developed and reported. Such models are either empirical in nature or semi-theoretical. The fact that our lack of knowledge of the structure of liquids hinders any advances that can be made in developing a successful theoretical model. Kendall and Monroe (2002) proposed a model for the non-polar and non-associated systems. Panchenkov (1950) reported a correlative equation for the viscosity of fluids by using empirical coefficient and energy bond parameter between components. Grunberg and Nissan (1950) presented a correlative viscosity model by adding interaction binary parameter that depends on the compositions of components. On the other side, local-composition models represent powerful tools can be used for the prediction of multi-component systems, specifically for the heavier solutions like polymeric mixtures and ionic liquids. Wilson, NRTL and UNIQUAC are the main local-composition models for the correlation and prediction of different properties of mixtures.

The McAllister viscosity model (1960) is another empirical model which has been successful for calculating viscosities over the entire composition range.. McAllister (1960) developed his correlative model assuming three-body (3b) and four-body (4b) collision of molecules. McAllister's 4b model is more complicated than the 3-b model as it has more binary interaction types. The capability of the McAllister 3b-model (Mc-3b) indicated that this model can correlate the binary systems with radii ratio of components of less than 1.5. For radii ratios higher than 1.5, McAllister (1960) suggested employing his 4b (Mc-4b) collision model. Noda *et al*. (1983) reported a five-body (5b) McAllister interaction model and employed it to calculate the dependence of viscosities of aqueous solutions.

In the present work, new mixing rules are being proposed for *pseudo*-binary McAllister model, which the present author believes that they will improve the prediction of *pseudo*-binary McAllister models. In addition, the correlative McAllister interaction 5b model is converted into a predictive model for regular binary systems. A comparison of the results of testing the proposed model are compared with the results obtained for the other versions of the McAllister model.

4.2. Modelling

4.2.1. Converting the McAllister 5b into a predictive model

Chapters 3 and 4 of the present work showed the improvement in the prediction of the dependence of viscosities of binary regular mixtures when the McAllister four-body model is used. The McAllister 5b (Mc-5b) is converted into a predictive model. Noda *et al.* (1983) developed a McAllister-type model on the basis of the collision of 5 neighboring molecules. They obtained Mc-5b viscosity model and it can be rewritten as:

$$Ln\, v_{mix} = x_1^5 ln\, v_1 + \frac{M_2}{M_1} x_2^5 ln\, v_2 + 5(x_1^4 x_2 ln\, v_{11112} \frac{4+\frac{M_2}{M_1}}{5} + x_1^4 x_2 ln\, v_{22221} \frac{4\frac{M_2}{M_1}+1}{5}) + 10(x_1^3 x_2^2 ln\, v_{11122} \frac{3+2\frac{M_2}{M_1}}{5} + x_2^3 x_1^2 ln\, v_{22211} \frac{3\frac{M_2}{M_1}+2}{5}) - ln \frac{M_{mix}}{M_1} \quad (4.1)$$

where x_i and M_i are the mole-fraction and the molecular weight of components, respectively. v_1 and v_2 are the kinematic viscosities of the pure components, respectively.

The v_{11112} and v_{22221} are, the, binary type 1 interaction parameters. , v_{11122} and v_{22211} are the binary type 2 interaction parameters. In order to make this model predictive, the Asfour *et al*. (1991) technique is utilized here. Data of the binary systems: toluene + decane (Vavanellos *et al.* 1991), toluene + dodecane, toluene + tetradecane and toluene + hexadecane (Asfour *et al*. 1990) were used to determine the values of the parameters, Values of the dimensionless lumped parameter, $\frac{v_{ij}^{(I)}}{(v_i^4 v_j)^{0.2}}$ were plotted against $\frac{(N_j-N_i)^2}{(N_i^4 N_j)^{0.2}}$ as depicted in Figure (4.1), w here N_i and N_j are the effective carbon numbers, *ECN*, of components i and j, respectively. The same approach is applied to both binary interaction type 1 leading to the same equations. According to Figure (4.1c), binary interaction type 1 parameter is obtained with the help of the following equation:

$$Ln\ \frac{v_{ij}^{(I)}}{(v_i^4 v_j)^{0.2}} = 0.924 + 0.037\frac{(N_j - N_i)^2}{(N_i^4 N_j)^{0.2}} \tag{4.2}$$

According to Figures (4.1b and c), binary types 1 and 2 are depicted. Equation (3) and (4) are obtained as follows:

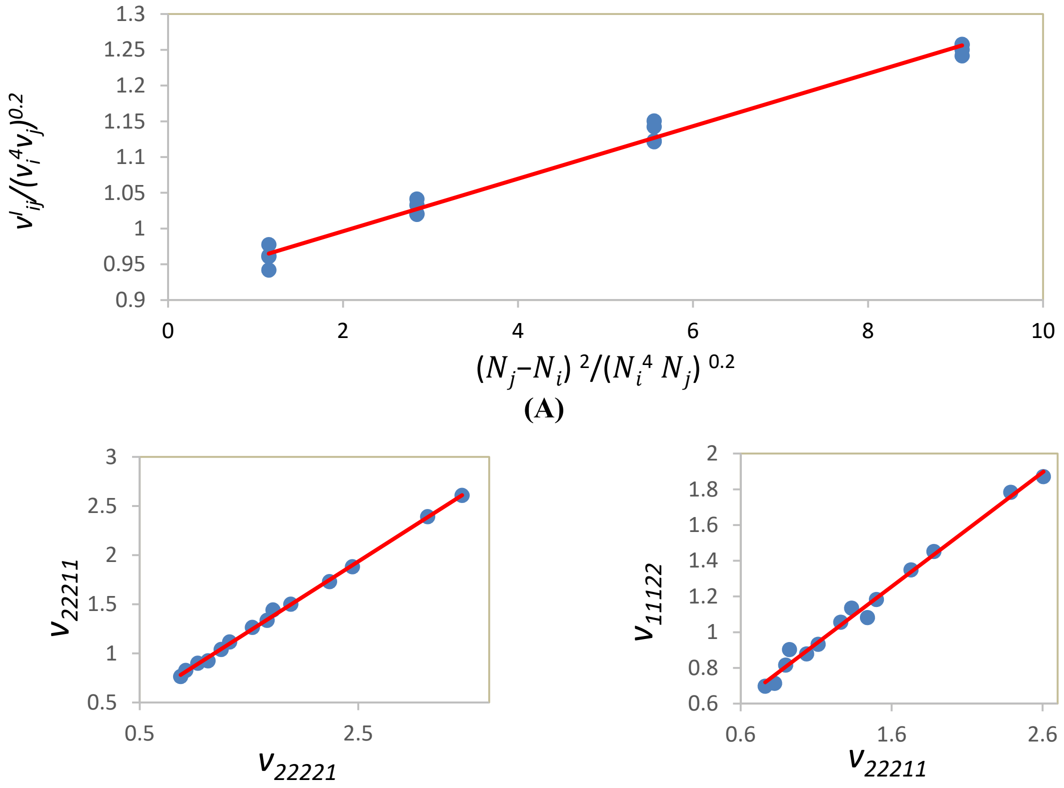
$$v_{22211} = 0.7135\, v_{22221} + 0.0168 \tag{4.3}$$

$$v_{11122} = 0.633\, v_{22211} + 0.2276 \tag{4.4}$$

As can be seen, the equations are derived in a slightly different manner than in the cases of the 3b abd 4b models. It should also be pointed-out here that the 3b and 4b collision models, contain a number of interaction parameters that is lower than the 5b model.

4.2.2. The McAllister *pseudo*-binary models

Extending the McAllister interaction models to the multi-component mixtures would result in an increase in the number of interaction parameters since the number of constituent components in solutions increases. Wu and Asfour (1992) proposed a *pseudo*-binary model to resolve the issue of the increased number of parameters. The *pseudo*-binary model reduces the number of parameters to two regardless of the number of components in a mixture.



(A)

(B)

(C)

Figure 4.1. (a) Variation of the lumped parameter, $v_{ij}^{(I)}/(v_i^4 v_j)^{0.2}$, with the term, $(N_j - N_i)^2/(N_i^4 N_j)^{0.2}$, as a function of the effective carbon number of components (b) Variation of the v_{22211} parameter with the v_{22221} parameter values, (c) Variation of v_{11122} parameter with the v_{22211} parameter values.

The *pseudo*-binary model was also employed with the Mc-3b model (Nhaesi and Asfour, 2000b) for regular and *n*-alkane systems. The same approach was employed with the Mc-4b model, as was explained in Chapter 3 of the present work The hypothetical system of one quaternary system is depicted in Figure (4.2) on the basis of the *pseudo*-binary model..

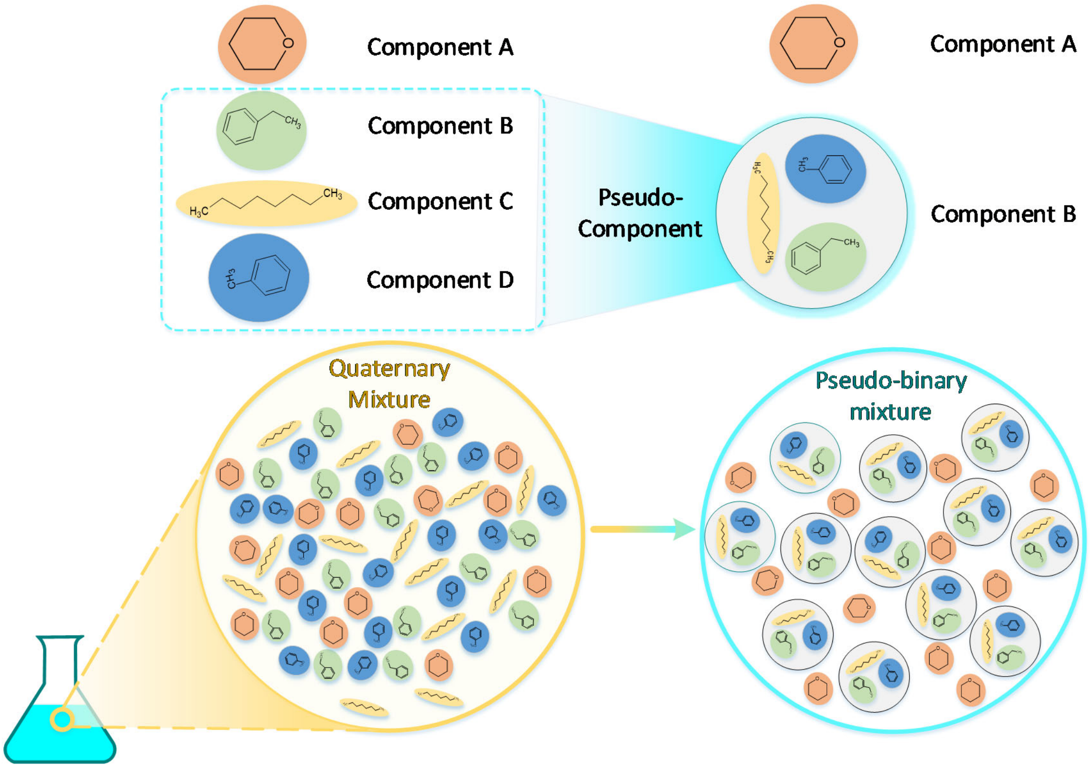


Figure 4.2. A hypothetical *pseudo*- binary system of a multi-component mixture.

Using the McAllister models with the *pseudo*-binary model, Equations (4.5) through (4.9) are used,

$$\ln v_i = -1.943 + 0.193\, N_i \tag{4.5}$$

$$(N)_{2'} = \sum_{i=2}^{n} X_i N_i \tag{4.6}$$

$$Ln\, v_{2'} = \sum_{i=2}^{n} X_i \ln v_i \tag{4.7}$$

$$Ln\, M_{2'} = \sum_{i=2}^{n} X_i \ln M_i \tag{4.8}$$

$$X_i = \frac{x_i}{\sum_{i=2}^{n} x_i} \tag{4.9}$$

where N_i, v_i, M_i and x_i are the effective carbon numbers, kinematic viscosity, molecular weight and mole-fraction of component *i* in a liquid mixture, respectively. The normalized mole-fraction, X_i, is used instead of x_i to determine the value of the *pseudo*-component parameters.

4.2.3. The interaction parameters of the Mc-3b model

Nhasi and Asfour (2000a) suggested to use following relations to calculate interaction parameters,

$$\frac{v_{12}}{({v_1}^2 v_2)^{\frac{1}{3}}} = 0.044\frac{(N_2 - N_1)^2}{({N_1}^2 N_2)^{\frac{1}{3}}} + 1 \tag{4.10}$$

$$v_{21} = v_{12}(\frac{v_2}{v_1})^{1/3} \tag{4.11}$$

4.2.4. The interaction parameters of the Mc-4b model

There are three interaction parameters which are classiffied into two categories for this model. It is proposed in the present work to use the following equations for the interaction parameters jn the present work::

$If\ (\Delta N < 3)$

$$\frac{v_{12}^I}{(v_1 v_2)^{\frac{1}{2}}} = 0.044\frac{(N_2 - N_1)^2}{(N_1 N_2)^{\frac{1}{2}}} + 1 \tag{4.12}$$

$If\ (\Delta N > 3)$

$$\frac{v_{12}^I}{(v_1 v_2)^{\frac{1}{2}}} = 0.09\frac{(N_2 - N_1)^2}{(N_1 N_2)^{\frac{1}{2}}} + 1 \tag{4.13}$$

$$v_{12}^{II} = v_{12}^I(\frac{v_1}{v_2})^{1/4} \tag{4.14}$$

$$v_{21}^{II} = v_{12}^I(\frac{v_2}{v_1})^{1/4} \tag{4.15}$$

where ΔN is the difference of effective carbon numbers of the largest and smallest components in a liquid mixture. In molecular thermodynamic modelling, exact values of interaction parameters are crucially important for determining the thermodynamic properties of systems. Therefore, an attempt to improve the predictive capability of the models by proposing new relationships to calculate the *pseudo*-binary interaction parameters.

It should be indicated here that the Mc-5b is not investigated here as a *pseudo*-binary model as long as the model cannot be functional for the multi-component systems. This issue is caused by the existing adjustable parameters of the model. The Mc-5b model was converted to a predictive model using a technique that is slightly different from what was done before with the other McAllister models. Equations (4.3) and (4.4) are compatible with binary regular systems while they cannot predict *pseudo*-binary interactions very well. This issue stems from the fact that the second component, the *pseudo*-component, is larger than the first component. It is expected that the deviation of the Mc-5b model from experimental data increases for the systems containing additional component. For example, in order to model the quinary systems using the Mc-5b model, Equations (4.3) and (4.4) are incompatible with the multi-component mixtures and need to be modified for the prediction which is not recommended as this will make the model complicated and inapplicable.

4.2.5. A New method to determine the interaction parameters of the pseudo-binary McAllister viscosity models

Originally, the interaction parameters for the *pseudo*-binary systems are calculated on the basis of Equations (4.12) through (4.15) that use the *pseudo*-component properties. Herein, it is suggested to calculate all binary interaction between component (1) and i to evaluate more precisely the *pseudo*-binary interaction parameters on the basis of the equations that follow instead of applying Equation (4.7). The value of the interaction between component 1 and the *pseudo*-component 2 is corresponding to the mole fraction of components 2, 3, …, n.

$$Ln\, v_{12}{}' = \sum_{i=2}^{n} X_i \ln v_{1i} \tag{4.16}$$

where $v_{12}{}'$ is the binary interaction parameter between component (1) and *pseudo*-component (2) which can be any type of binary parameter. For example, the *pseudo*-binary interaction can be calculated for ternary mixtures as follows:

$$Ln\, v_{12}' = X_2 \ln v_{12} + X_3 \ln v_{13} \tag{4.17}$$

$$v_{21}' = v_{12}' (\frac{v_2}{v_1})^{1/3} \tag{4.18}$$

where v_{12}' can be a representation of any type of binary interactions in the McAllister models. The predictive capabilities of the new technique and former one are compared over the entire composition range for multi-component mixtures. It should be noted here that the percentage of the absolute average relative deviation, *% AAD*, is used here to compare all models against each other.

$$\%AAD = \frac{1}{n} \sum_{i=1}^{n} \frac{\left| v_i^{exp} - v_i^{cal} \right|}{v_i^{exp}} \text{x100} \tag{4.19}$$

The symbols v_i^{exp} and v_i^{cal} represent the experimental and calculated kinematic viscosities, respectively.

4.3. Results and Discussions

The proposed models are validated using data of systems containing regular components and compared with each other with the *% AAD* used as a criterion for comparison.

4.3.1. Testing the predictive capability of Mc-5b model using binary systems data

The properties of pure componenst were obtained from the literatures. The Mc-5b model is tested and the % AAD is reported in Table 4.1. It was concluded earlier that the predictive capability of the Mc-4b was better than that for the Mc-3b for the binary regular systems. On the basis of the overall value of *%AAD,* the 5-body collision predictive version of the McAllister model appears to perform slightly better than the 3-body and 4-body interaction versions, viscosity models commonly show weaknesses on the regular systems containing general cyclic compounds, like cyclohexane or cyclooctane. Al-Gherwi, 2005 suggested multiplying the calculated effective carbon number [*ECN*] by 0.75 since the equation reported by Nhaesi and Asfour (1998) tends to over estimate the *ECN* for cyclic compounds. Al-Gherwi (2005) attributed that overestimation to the nature of the shap and structure of the cyclic compounds. Careful analysis of the results shows that in most binary systems containing cyclohexane and cyclooctane, the Mc-5b model performed well whereas the Mc-4b and the GC-UNIMOD experienced a difficulty predicting the viscosities of these systems. Figure (4.3) depicts the performance of four different models for the prediction of kinematic viscositis of the ethylbenzene + hexadecane at different temperatures. Because the GC-UNIMOD shows the highest deviation, it was removed from the figure to clrealy show the comparison between three McAllister models. According to Figure (4.3), the same trend is seen for the Mc-5b relative to the Mc-4b model. Mc-5b model conforms very closely to the experimental points. It is observed also from Figure (4.3) that increasing the temperature, enhances the predictive capability of the Mc-5b. Therefore, the Mc-5b model can be used for regular binary systems with larger *ECN* differences.

Table 4.1. Results of testing the predictive capability of the two types of McAllister investigated models using the binary experimental viscosity data of regular mixtures

Systems	**Ref**	**T [K]**	**% AAD**			
			GC-UNIMOD[1]	**3b[1]**	**4b[1]**	**5b**
cyclohexane (1) + ethylbenzene (2)	(Al-Gherwi, 2005)	293	11.15	3.99	5.88	2.51
		298	11.12	3.57	5.46	2.14
		308	9.63	2.44	4.26	1.52
		313	9.11	2.00	3.81	1.21
cyclohexane (1) + toluene (2)	(Al-Gherwi, 2005)	293	8.46	4.08	5.94	2.40
		298	8.62	3.79	5.64	1.88
		308	7.04	2.74	4.59	1.23
		313	6.91	2.23	4.02	1.07
heptane (1) + cyclohexane (2)	(Al-Gherwi, 2005)	293	6.71	2.56	4.34	5.39
		298	5.77	1.91	3.52	5.02
		308	5.72	1.54	3.18	5.67
		313	5.39	1.34	2.82	5.80
heptane (1) + ethylbenzene (2)	(Al-Gherwi, 2005)	293	4.53	1.39	0.39	1.01
		298	4.16	1.70	0.39	1.31
		308	3.62	2.14	0.75	2.09
		313	3.51	2.23	0.84	2.53
heptane (1) + toluene (2)	(Al-Gherwi, 2005)	293	3.39	1.55	0.42	1.11
		298	3.24	1.66	0.42	1.67
		308	3.11	2.22	0.49	2.37
		313	2.85	2.29	0.56	2.89
octane (1) + cyclohexane (2)	(Al-Gherwi, 2005)	293	5.25	2.42	4.16	2.47
		298	4.36	1.78	3.29	2.17
		308	3.95	1.31	2.25	2.08
		313	3.63	1.78	1.93	2.17
octane (1) + ethylbenzene (2)	(Al-Gherwi, 2005)	293	4.26	1.97	0.37	1.29
		298	4.24	2.00	0.44	1.78
		308	3.52	2.56	0.86	1.09
		313	3.24	2.78	1.08	0.72
octane (1) + toluene (2)	(Al-Gherwi, 2005)	293	3.68	1.87	0.44	2.34
		298	3.65	1.94	0.45	1.70
		308	3.06	2.61	0.94	1.04
		313	2.90	2.76	1.09	0.56
toluene (1) + ethylbenzene (2)	(Al-Gherwi, 2005)	293	9.96	6.10	4.68	5.18
		298	9.43	5.94	4.51	4.39
		308	8.88	6.00	4.58	3.16
		313	8.62	6.02	4.59	2.58
m-Xylene (1) + decane (2)	(Al-Gherwi, 2005)	308	0.56	1.73	2.48	0.64
		313	0.53	1.79	2.57	0.75
cyclohexane (1) + m-Xylene (2)	(Al-Gherwi, 2005)	308	9.15	2.06	4.03	2.28
		313	8.84	1.83	3.75	1.96
cyclohexane (1) + cyclooctane (2)	(Al-Gherwi, 2005)	308	1.18	0.95	0.76	3.53
		313	0.73	0.78	1.43	2.72
cyclohexane (1) + chlorobenzene(2)	(Al-Gherwi, 2005)	308	5.56	1.22	1.00	4.54
		313	5.99	0.99	1.49	3.60
chlorobenzene (1) + decane (2)	(Al-Gherwi, 2005)	308	0.77	1.62	0.58	0.81
		313	0.23	2.02	0.70	0.46
ethylbenzene (1) + n-tetradecane (2)	(Vavanellos *et al.* 2002)	293	8.36	1.76	0.80	0.54
		298	7.59	0.90	0.68	0.62
	(Asfour *et al.*, 2002)	308	5.95	1.00	0.52	0.73
		313	5.43	2.09	0.54	0.60
ethylbenzene (1) + n-hexadecane (2)	(Vavanellos *et al.* 2002)	293	10.62	3.74	1.35	1.20
		298	9.69	3.75	1.14	1.02
	(Asfour *et al.* 2002)	308	7.75	3.60	1.18	0.84
		313	6.98	3.56	1.35	0.79
Overall			5.60	2.45	2.21	**2.09**

4.3.2. Testing the predictive capability of the modified *pseudo*-binary McAllister models for the multi-component systems

The *% AAD* of four *pseudo*-binary McAllister models are reported in Tables 4.2 through 4.4. The results reported in Table 4.2 are for ternary systems, the results reported in Table 4.3 are for quaternary systems and finally the results reported in Table 4.4 are for quinary systems. It is clear from the results reported in the aforementioned tables that the *pseudo*-binary modified Mc-4b predicts viscosity with lower %AAD than both the Mc-3b and the Mc-4b. The proposed technique improved the result of Mc-3b-*pseudo* and Mc-4b-*pseudo* models. The overall result of the modified Mc-4b-*pseudo* (M-4b-*pseudo*) and modified Mc-3b-*pseudo* (M-3b-*pseudo*) give the following results in terms of %AAD: 3.38 and 2.57, respectively. The technique improves the result of 4b-Pseudo model on the ternary systems slightly. In Chapter 3, it was reported that the, 4b-*pseudo*-binary model performed better in the case of the ternary systems than the original McAllister 4b multi-component model. However, it appears that the proposed technique improves predictions for all kinds of systems. The new mixing showed a slight change in the case of some of the ternary systems, however clearer improvement can be seen in systems with larger number of components forming the *pseudo*-component. For example, for most of the ternary systems containing tetradecane and hexadecane, the proposed technique inproves the predictive capability by about 50%. Considering a multi-component system as a *pseudo*-binary systems, the kinematic viscosity can be envisaged to vary as a light component. For example, the kinematic viscosity of the system: toluene (1) + ethylbenzene (2) + hexadecane (3), is shown in Figure (4.4) on the basis of of the lightest component mole-fractions. According to the plots of M-3b and M-4b *pseudo*-binary models, the M-4b-*pseudo*-binary model precisely fits the data. Considering the system at the specific temperature, the highest inaccuracy of prediction can be seen at the point when the plot hits the max kinematic viscosity. The *pseudo*-binary systems are at its maximum when the composition of second component, *pseudo*- component, is high at a certain low level of

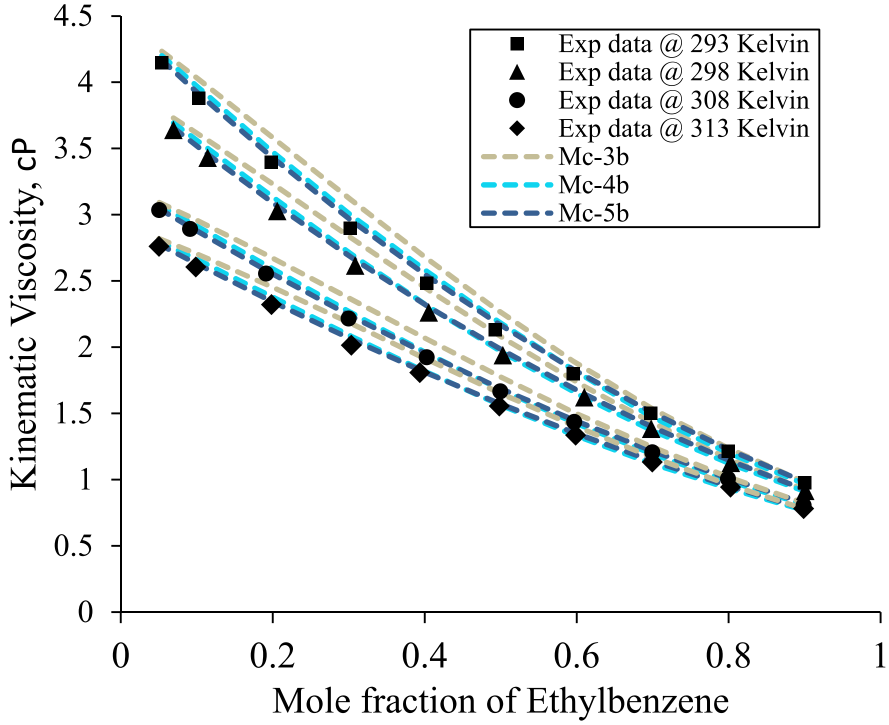


Figure 4.3. Performance of three different models for predicting the kinematic viscosity of the ethylbenzene + hexadecane at different temperatures.

first component composition. According to Figure (4.4) a comparison of the 4b-*pseudo*-binary model between 293 K and 313 K, it can be observed that the models conform more closely to experimental data as the temperature increases.

Table 4.2. Results of testing the predictive capability of the *pseudo*-binary McAllister models using the ternary experimental viscosity data of various regular mixtures.

Systems	**Ref**	**T [K]**	**% AAD**			
			3b-*Pseudo*	**M-3b-*Pseudo***	**4b-*Pseudo***	**M-4b-*Pseudo***
toluene (1) + octane (2) + ethylbenzene (3)	(Nhaesi, 1998)	293	3.28	2.75	0.43	0.77
		298	3.22	2.69	0.74	1.25
		308	1.71	1.40	2.06	3.15
		313	3.11	2.50	0.83	1.21
toluene (1) + octane (2) + tetradecane (3)	(Nhaesi, 1998)	293	2.35	1.01	2.25	2.52
		298	2.26	1.08	2.46	2.47
		308	2.39	1.56	2.39	2.20
		313	1.76	1.41	4.08	3.18
toluene (1) + octane (2) + hexadecane (3)	(Nhaesi, 1998)	293	5.85	3.38	2.80	3.07
		298	5.65	3.53	2.73	3.00
		308	4.94	3.61	2.70	2.95
		313	4.43	3.59	2.68	2.92
toluene (1) + ethylbenzene (2) + tetradecane (3)	(Nhaesi, 1998)	293	2.23	0.88	2.05	2.67
		298	2.40	1.19	2.12	2.40
		308	2.31	1.52	2.04	2.07
		313	2.09	1.56	2.06	2.11
toluene (1) + ethylbenzene (2) + hexadecane (3)	(Nhaesi, 1998)	293	5.83	3.72	3.74	2.99
		298	5.86	3.92	3.92	2.86
		308	5.58	4.13	4.15	2.94
		313	5.17	4.04	3.98	2.69
toluene (1) + tetradecane (2) + hexadecane (3)	(Nhaesi, 1998)	293	0.89	0.33	0.84	0.84
		298	0.67	0.30	0.76	0.75
		308	0.9	0.38	0.82	0.8
		313	1.42	0.42	0.83	0.81
octane (1) + ethylbenzene (2) + tetradecane (3)	(Nhaesi, 1998)	293	0.87	0.66	1.33	2.00
		298	1.25	0.86	1.73	1.79
		308	1.76	0.99	1.78	1.54
		313	1.83	0.94	1.81	1.59
octane (1) + ethylbenzene (2) + hexadecane (3)	(Nhaesi, 1998)	293	3.00	2.09	2.77	1.96
		298	3.52	2.38	3.13	2.06
		308	3.84	2.44	3.2	2.25
		313	4.02	2.48	3.14	2.23
ethylbenzene (1) + tetradecane (2) + hexadecane (3)	(Nhaesi, 1998)	293	0.42	0.75	0.52	0.54
		298	0.35	0.37	0.42	0.40
		308	1.12	0.27	0.45	0.43
		313	1.64	0.18	0.6	0.56
octane (1) + heptane (2) + ethylbenzene (3)	(Elhadad, 2005)	293	3.04	2.73	1.86	1.81
		298	2.87	2.57	1.97	1.92
octane (1) + heptane (2) + toluene (3)	(Elhadad, 2005)	293	3.50	3.15	1.60	1.59
		298	7.00	6.21	3.51	3.50
octane (1) + ethylbenzene (2) + toluene (3)	(Elhadad, 2005)	293	0.69	0.62	3.01	2.98
		298	3.35	2.97	0.81	0.79
octane (1) + heptane (2) + cyclohexane (3)	(Elhadad, 2005)	293	6.79	5.98	2.96	2.96
		298	6.34	5.58	2.64	2.64
heptane (1) + ethylbenzene (2) + cyclohexane (3)	(Elhadad, 2005)	293	5.70	4.69	1.62	1.63
		298	9.59	8.43	5.13	5.14
octane (1) + ethylbenzene (2) + cyclohexane (3)	(Elhadad, 2005)	293	10.03	8.64	5.20	5.21
		298	9.19	7.97	4.47	4.48
heptane (1) + cyclohexane (2) + toluene (3)	(Elhadad, 2005)	293	11.64	9.74	6.64	6.65
		298	4.47	3.84	5.81	5.79
ethylbenzene (1) + cyclohexene (2) + toluene (3)	(Elhadad, 2005)	293	8.70	7.56	4.99	4.97
		298	8.05	6.99	4.53	4.51
hexane (1) + ethylbenzene (2) + octane (3)	(Al-Gherwi, 2005)	293	6.14	5.98	5.85	5.25
		298	8.09	8.03	8.31	7.56
hexane (1) + toluene (2) + octane (3)	(Al-Gherwi, 2005)	293	3.94	3.57	1.17	0.85
		298	3.72	3.49	1.09	0.82
hexane (1) + cyclohexane (2) + octane (3)	(Al-Gherwi, 2005)	293	7.51	6.68	3.81	3.51
		298	6.94	6.30	3.38	3.09
hexane (1) + cyclohexane (2) + ethylbenzene (3)	(Al-Gherwi, 2005)	293	9.66	8.28	5.93	5.66
		298	8.95	7.91	5.41	5.25
hexane (1) + toluene (2) + ethylbenzene (3)	(Al-Gherwi, 2005)	293	4.13	3.09	0.34	0.29
		298	4.60	3.81	1.00	0.91
Overall			4.27	**3.38**	2.69	**2.57**

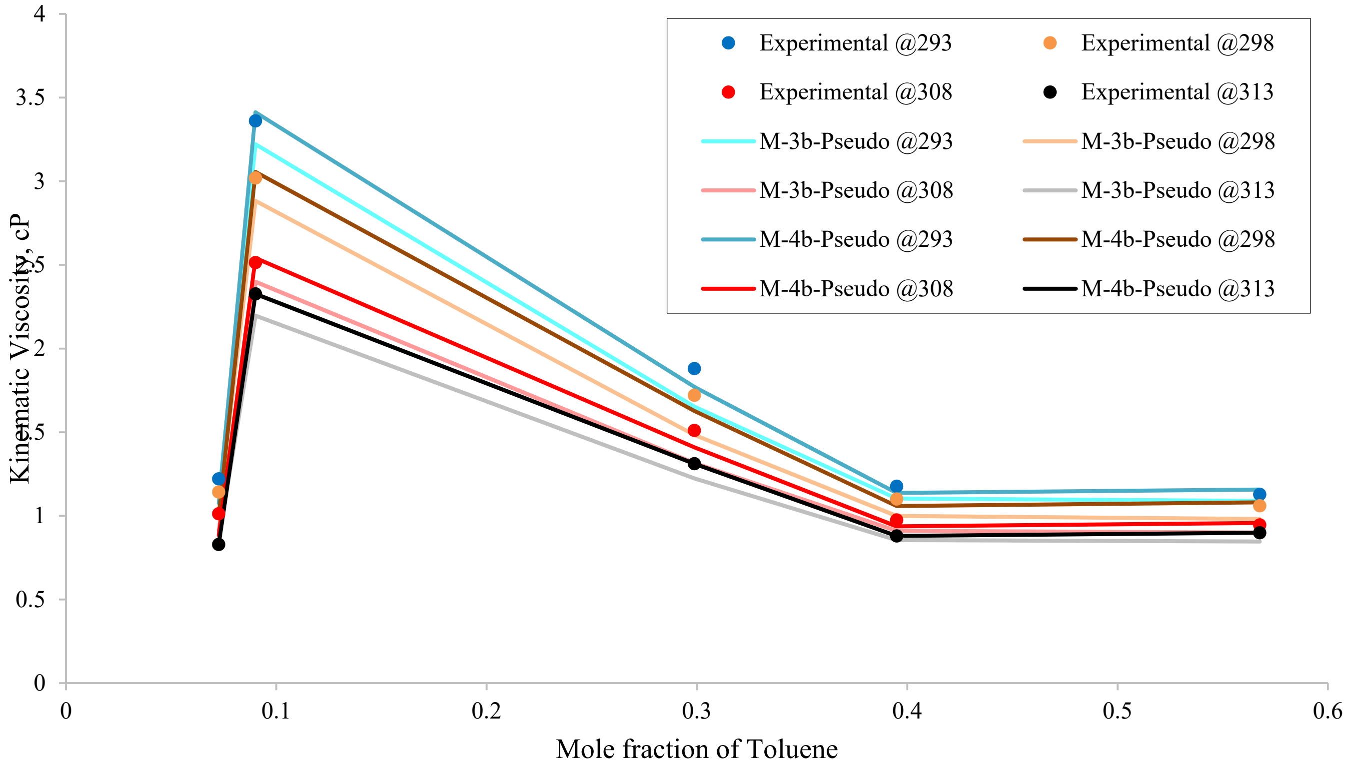


Figure 4.4. Kinematic viscosity behavior of *pseudo*-binary system of toluene (1) + ethylbenzene (2) + hexadecane (3) based on the variation of light component composition along with the predictive capability of the Mc-*pseudo*-binary models.

For the quaternary systems, a similar trend to that of the ternary systems was observed. In most of the systems, the new technique reduces the deviation from experimental data. The overall percentage error confirms the applicability of the new technique to find the exact intermolecular interactions for the *pseudo*-binary models. Similar to the ternary systems, the M-4b-*pseudo* increases the accuracy of prediction, but not by much; however, it can be seen that the technique is successfully applicable especially in the cases of components containing larger molecules, such as tetradecane and hexadecane. As for the systems with smaller molecules, the M-4b-*pseudo* was not effective while the suggested mixing rule enhances the predictive capability of the McAllister *pseudo*-binary model with three collision of molecules. With regard to quinary systems, in almost all systems the new technique improved the predictive capability of the models. For example, for the system: toluene (1) + octane (2) + ethylbenzene (3) +tetradecane (4) + hexadecane (5), the new technique of predicting the interaction parameters increases the predictive capability of the 4b and 3b *pseudo*-binary models at different temperatures. For the system: octane (1) + hexane (2) + ethylbenzene (3) + cyclohexane (4) + toluene (5), the new technique of prediction improves the predictive capability by 50% for the 4b-*pseudo*-binary model while it was not effective when applied to the 3b-*pseudo*-binary model. The same trend was observed for the system: cyclohexane (1) + *m*-Xylene (2) + cyclooctane (3) + chlorobenzene (4) + decan (5). One can thus conclude that the 4b-*pseudo*-binary model is more compatible with the system with larger *pseudo*- components like the quinary systems. Therefore, on the basis of the overall results of the quinary systems, the M-4b-*pseudo* with a %AAD of 3.5 shows the best predictive capability over the other models. Moreover, the newly proposed technique forcalculating the *pseudo*-binary interaction parameters is showing more compatibility with 4b-*pseudo*-binary model. Although the 4b-*pseudo*-binary model is generally better than the 3b-*pseudo*-binary model, the new technique makes the 3b-*pseudo*-binary model more accurate than the 4b-*pseudo*-binary model that is based on the old mixing rules. For example, it can be concluded that for the ternary system: toluene (1) + ethylbenzene (2) + hexadecane (3) or the quaternary system: toluene (1) + ethylbenzene (2) + tetradecane (3) + hexadecane (4) and the quinary system: toluene (1) + octane (2) + ethylbenzene (3) + tetradecane (4) + hexadecane (5), the M-3b-*peudo*-binary model conforms more closely to the experimental data than the original 4b-*pseudo*-binary model. In other words, Figure (4.5) depicts a disparity plot for the ternary system:toluene (1) + ethylbenzene (2) + hexadecane (3) along with the quaternary system: toluene (1) + ethylbenzene (2) + octane (3) + hexadecane (4) and the quinary system: toluene (1) + ethylbenzene (2) + octane (3) + hexadecane (4) + tetradecane (5) atdifferent temperatures. The diagonal line with 45^0 degree and the scattered plot represent the experimental data and the accuracy of models of those systems, respectively. Figure (4.6) depicts a comparison of the predictive capability of all the *pseudo*-binary models and their modified versions.

Table 4.3. Results of testing the predictive capability of the Pseudo-binary McAllister models using the Quaternary experimental viscosity data of various regular mixtures

Systems	**Ref**	**T [K]**	**%AAD**			
			3b-*Pseudo*	**M-3b-*Pseudo***	**4b-*Pseudo***	**M-4b-*Pseudo***
toluene (1) + octane (2) + ethylbenzene (3) + tetradecane (4)	(Nhaesi, 1998)	293	1.87	1.14	1.65	1.14
		298	2.29	1.54	1.91	1.49
		308	1.84	1.50	1.89	1.45
		313	2.15	1.81	2.39	1.78
toluene (1) + octane (2) + ethylbenzene (3) + hexadecane (4)	(Nhaesi, 1998)	293	5.03	3.68	2.73	3.41
		298	4.89	3.69	4.80	3.8
		308	4.72	3.85	4.98	3.95
		313	4.82	4.13	5.50	3.87
toluene (1) + ethylbenzene (2) + tetradecane (3) + Hexadecane (4)	(Nhaesi, 1998)	293	4.30	3.07	2.99	2.40
		298	4.29	3.23	3.23	2.64
		308	4.20	3.55	3.56	2.97
		313	4.14	3.72	3.75	3.17
octane (1) + ethylbenzene (2) + tetradecane (3) + hexadecane (4)	(Nhaesi, 1998)	293	2.11	1.88	2.57	2.52
		298	2.63	2.29	2.71	2.63
		308	2.81	2.33	2.71	2.63
		313	2.98	2.43	2.76	2.68
toluene(1) + octane (2) + tetradecane (3) + hexadecane (4)	(Nhaesi, 1998)	293	3.56	2.32	3.22	3.48
		298	3.43	2.51	3.19	3.35
		308	2.83	2.61	3.14	3.25
		313	6.78	6.58	4.50	4.15
octane (1) + hexane (2) + ethylbenzene (3) + Cyclohexane (4)	(Elhadad, 2005)	293	8.02	7.55	5.27	5.40
		298	7.51	7.07	4.78	4.90
octane (1) + hexane (2) + ethylbenzene (3) + toluene(4)	(Elhadad, 2005)	293	0.98	1.02	1.54	1.44
		298	3.63	3.49	1.32	1.25
octane (1) + heptane(2) + ethylbenzene (3) + Cyclohexane(4)	(Elhadad, 2005)	293	8.36	7.74	5.53	5.56
		298	7.81	7.25	5.02	5.04
octane (1) + heptane(2) + ethylbenzene (3) + toluene(4)	(Elhadad, 2005)	293	4.03	3.70	2.91	2.91
		298	3.67	3.32	2.95	2.94
octane (1) + heptane(2) + cyclohexane (3) + toluene(4)	(Elhadad, 2005)	293	8.09	7.54	5.54	5.55
		298	7.57	7.05	5.13	5.08
heptane (1) + ethylbenzene (2) + cyclohexane (3) + toluene(4)	(Elhadad, 2005)	293	9.19	8.49	6.42	6.43
		298	8.40	7.76	5.65	5.67
octane(1) + ethylbenzene (2) + cyclohexane (3) + toluene(4)	(Elhadad, 2005)	293	9.17	8.47	6.57	6.58
		298	8.52	7.88	6.10	5.96
cyclohexane (1) + m-Xylene (2) + cyclooctane (3) + chlorobenzene (4)	Hamzehlouia and Asfour, 2012)	308	8.10	7.57	5.53	5.83
		313	8.76	8.19	5.90	6.23
cyclohexane (1) + m-Xylene (2) + cyclooctane (3) + decane (4)	Hamzehlouia and Asfour, 2012)	308	8.31	7.73	5.55	5.85
		313	7.88	7.30	5.10	5.4
cyclohexane (1) + m-Xylene (2) + chlorobenzene (3) + decane (4)	Hamzehlouia and Asfour, 2012)	308	3.95	3.72	1.31	1.49
		313	3.78	3.53	1.22	1.39
cyclohexane (1) + cyclooctane (2) + chlorobenzene (3) + decane (4)	Hamzehlouia and Asfour, 2012)	308	6.34	5.90	3.33	3.6
		313	6.62	6.12	3.57	3.82
m-Xylene (1) + cyclooctane (2) + chlorobenzene (3) + decane (4)	Hamzehlouia and Asfour, 2012)	308	7.69	7.14	4.41	4.59
		313	7.78	7.16	4.50	4.61
Overall			5.36	**4.79**	3.85	**3.73**

Table 4.4. Result of testing the predictive capability of the *pseudo*-binary McAllister models using the quinary experimental viscosity data of various regular mixtures

System	**Ref**	**T (K)**	**%AAD**			
			3b-*Pseudo*	**M-3b-*Pseudo***	**4b-*Pseudo***	**M-4b-*Pseudo***
toluene (1) + octane (2) + ethylbenzene (3)+ tetradecane (4) + hexadecane (5)	(Nhaesi, 1998)	293	4.52	3.83	3.75	3.44
		298	4.36	3.94	2.738	2.38
		308	4.22	3.89	3.95	3.07
		313	2.89	2.63	3.02	2.67
octane (1) + hexane (2) + ethylbenzene(3) + cyclo hexane(4) + toluene (5)	(Elhadad, 2005)	293	5.73	6.18	5.96	3.27
		298	5.35	5.93	5.55	2.88
cyclohexane (1) + *m*-xylene (2) + cyclooctane (3)+ chlorobenzene (4) + decane (5)	(Hamzehlouia and Asfour, 2012)	308	7.52	7.43	7.84	5.33
		313	7.2	7.22	7.51	5.02
Overall			5.22	**5.13**	5.03	**3.50**

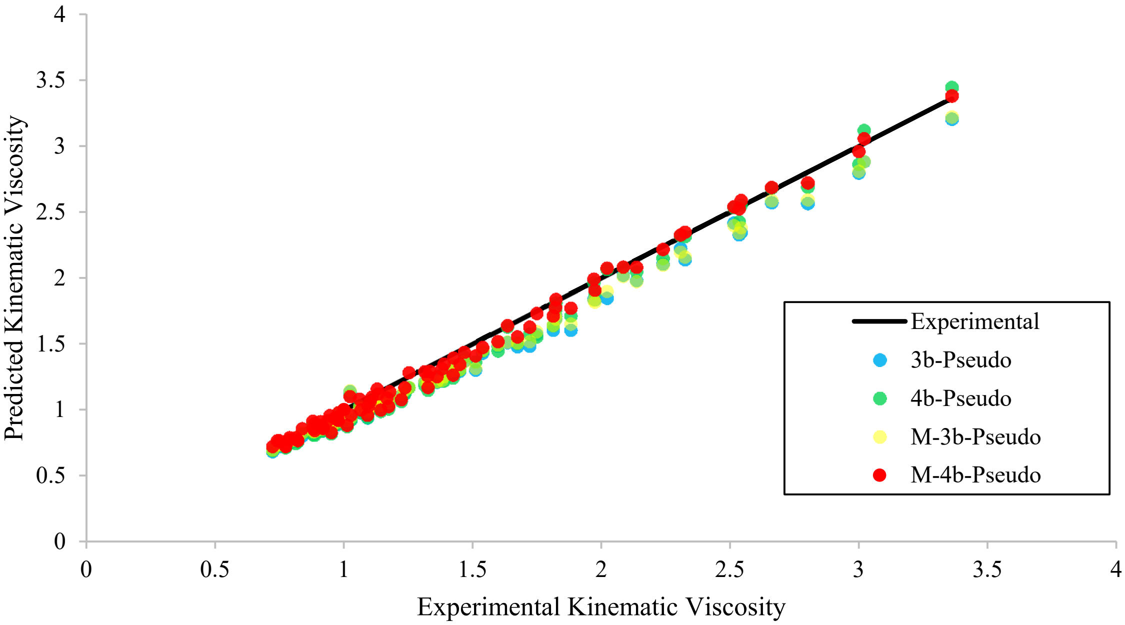


Figure 4.5. Comparison between experimental and calculated kinematic viscosity of various models for the ternary, quaternary and quinary systems containing (toluene, octane, ethylbenzene, tetradecane, hexadecane).

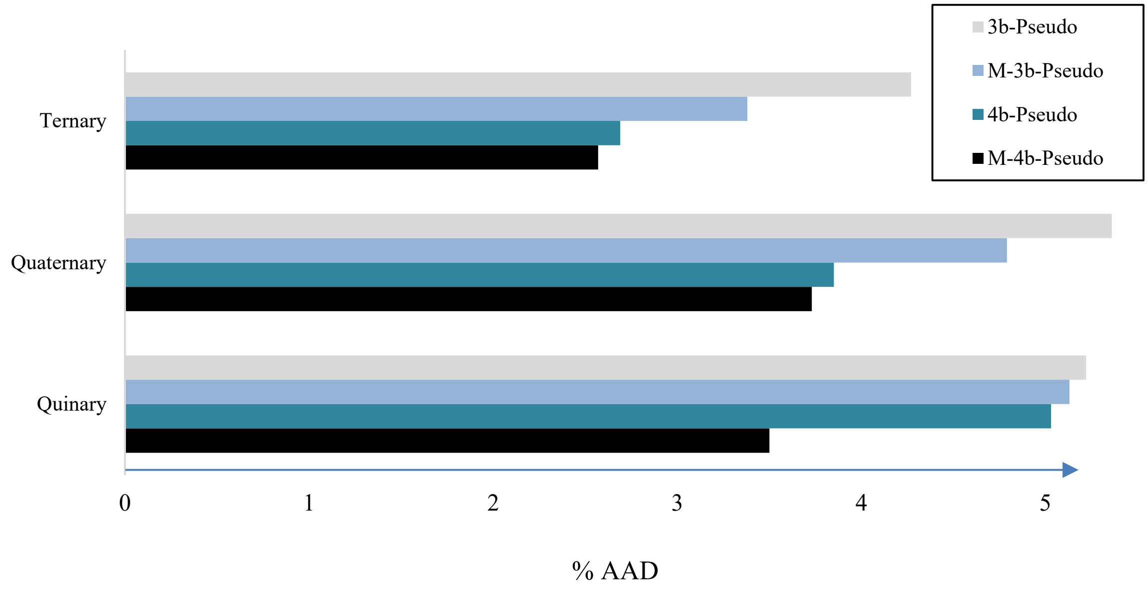


Figure 4.6. Comparative plots which illustrate the performance of the Mc-3b-*pseudo*, the M-3b-*pseudo,* the Mc-*pseudo*-4b. and the M-4b-*pseudo* models

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The work reported herein is mainly focused on the predictive capability of the McAllister model for the prediction of kinematic viscosity of multi-component systems over the entire composition range. Subsequently, in the first part of the study, Chapter 3, in addition to generalizing the McAllister 4-body model from binary to the multicomponent systems, The Asfour *et al*. (1991) technique was applied to convert the McAllister correlative model into a predictive one.. Then, four subset models of McAllister's (3b, 3b-*pseudo*, 4b and 4b-*pseudo*) and the GC-UNIMOD were compared together.

In the first part of the study, Chapter 3, the binary, ternary, quaternary and quinary system prediction results for the regular systems with no n-akanol components were reported. It was concluded that if the number of carbon difference between two components, one with the maximum number of carbon and the second with the least number of carbon atoms, among all components of the system, has been more than three, the McAllister four-body will perform better than the McAllister three-body model. The *pseudo*-binary McAllister models showed more satisfactory results in the case of *n*- alkanes and 1-alkanol systems while it was expected to have more satisfactory results in original McAllister, three-body and four-body, models. This is mainly because of their simple kinematic viscosity behavior. For the *n*-alkane and *n*-akanol systems, it is suggested to use the simple model with less predictive interaction parameters because the values of interactions are depending on each other and predicting many parameters can cause more error in prediction. The aforementioned point is the main reason for the better performance of pseudo-binary models over their McAllister models in n-Alkane and n-Akanol systems. Pseudo-binary technique, except in the case of ternary systems, was not successful in improving the original McAllister models' performance for regular systems and systems containing regular components along with n-Akanol. This is mainly due to the complex thermodynamic behavior of those systems. Therefore, the new interaction parameters will be essential to have a more precise prediction.

In second part of study, Chapter 4, correlative Mc-5b model was converted to the predictive model and tested over the regular range of binary systems. For converting the model Asfour (1991) technique was used here to find the new proportional relation between the interaction parameters of Mc-5b model. The results showed the better performance of Mc-5b model over the other models for the binary regular mixtures with % AAD of 2.09. In addition, McAllister Pseudo-binary models 3b and 4b is used here to predict the kinematic viscosity of multicomponent mixtures. To improve the results for multicomponent systems, new technique is used to determine the Pseudo-binary interaction parameters of such models. In this technique, all binary interaction parameters between component *n* and component one, light component, would be calculated and utilized to determine the Pseudo-binary interaction parameters by the proposed relations. The obtained results show the suitability of new technique to improve the performance of McAllister Pseudo-binary models. It should be noted that the effectiveness of technique is more clear in points of system with high kinematic viscosity as long as the highest error is experienced in points with the high range of kinematic viscosity in *pseudo*-binary models.

5.2. **Recommendations**

In terms of future work, there are a number of areas worthy of further exploration. Nowadays, IONIC liquids and polymeric components, like polyethylene glycol (PEG) have been used vastly in pharmaceutical industry. Therefore, knowing the specific thermodynamic properties of mixtures containing these macromolecules are crucial important. Due to the unsymmetric shape of molecules, along with their positively or negatively charged part of them, the viscosity variation over the different compositions is highly complex. Since the McAllister model showed its strength for the correlation of complicated systems, it would be suitable to apply the McAllister model on this type of data. However, because of the complexity of such systems, regression or multi regression method would not be very helpful, so, It is expected to use other techniques, like ANN, to predict the intermolecular interactions between components for the McAllister model.

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VITA AUCTORIS

NAME: Amirhossein Amirsoleymani

PLACE OF BIRTH: Babol, Mazandaran, Iran

YEAR OF BIRTH: 1990

EDUCATION: Bachelor of Science in Chemical Engineering, (Process design), Babol Noshirvani University of Technology, Babol, Mazandaran, Iran, 2009-2015.

Master of Science in Chemical Engineering, (Thermo-kinetics and Catalyst), Babol Noshirvani University of Technology, Babol, Mazandaran, Iran, 2015-2018.

Master of Applied Science in Environmental Engineering, University of Windsor, M.A.Sc., Windsor, ON, Canada, 2019-2021.